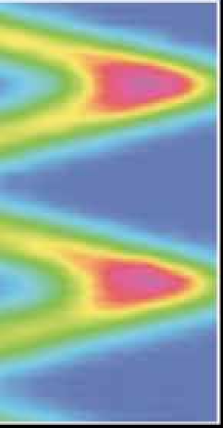

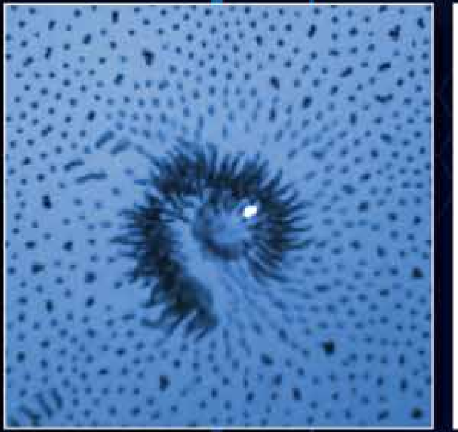

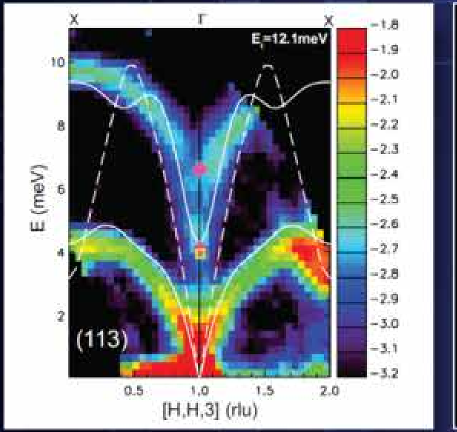

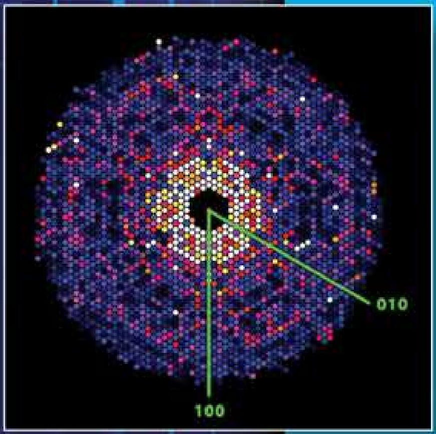

2011

Basic Energy Sciences
FY 2011 Research Summaries

U.S. DEPARTMENT OF ENERGY | Office of Science

Contents

Preface

This is a collection of summaries for more than 1300 research projects funded by the Office of Basic Energy Sciences (BES) in Fiscal Year 2011 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 inaugural 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 2011, 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. The *Basic Energy Sciences 2011 Summary Report* identifies the cover images and provides related research highlights.

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, UNIVERSITY OF BERKELEY
CALIFORNIA, UNIVERSITY OF DAVIS
CALIFORNIA, UNIVERSITY OF IRVINE
CALIFORNIA, UNIVERSITY OF LA
CALIFORNIA, UNIVERSITY OF MERCED
CALIFORNIA, UNIVERSITY OF RIVERSIDE
CALIFORNIA, UNIVERSITY OF SAN DIEGO
CALIFORNIA, UNIVERSITY OF SANTA BARBARA
CALIFORNIA, UNIVERSITY OF SANTA CRUZ
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
CLARK 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
JOHNS HOPKINS UNIVERSITY
KANSAS, UNIVERSITY OF
KANSAS STATE UNIVERSITY
KENT STATE UNIVERSITY
KENTUCKY, UNIVERSITY OF
LEHIGH UNIVERSITY
LOUISIANA STATE UNIVERSITY
MARINE BIOLOGICAL LABORATORY
MARYLAND, UNIVERSITY OF
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
MASSACHUSETTS, UNIVERSITY OF
MIAMI UNIVERSITY
MICHIGAN STATE UNIVERSITY
MICHIGAN TECHNOLOGICAL UNIVERSITY
MICHIGAN, UNIVERSITY OF
MINNESOTA, UNIVERSITY OF
MISSISSIPPI STATE UNIVERSITY
MISSOURI UNIVERSITY OF SCIENCE
MISSOURI, UNIVERSITY OF
MONTANA STATE UNIVERSITY

NATIONAL AERONAUT & SPACE ADM
NATIONAL INST OF STDS & TECH
NEBRASKA, UNIVERSITY OF
NEVADA, UNIVERSITY OF
NEW JERSEY INSTITUTE OF TECH
NEW MEXICO STATE UNIVERSITY
NEW MEXICO, UNIVERSITY OF
NEW YORK UNIVERSITY
NEW YORK, CITY UNIVERSITY OF CITY COLLEGE
NEW YORK, CITY UNIVERSITY OF HUNTER C.
NEW YORK, CITY UNIVERSITY OF LEHMAN C.
NEW YORK, CITY UNIVERSITY OF QUEENS C.
NEW YORK, STATE UNIVERSITY OF BINGHTN
NEW YORK, STATE UNIVERSITY OF BUFFALO
NEW YORK, STATE UNIVERSITY OF ST BROOK
NEW YORK, STATE UNIVERSITY OF SYRACUSE
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, 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
RUTGERS - STATE UNIV OF NJ
SALK INSTITUTE FOR BIOLOGICAL STUDIES
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, UNIV. OF HEALTH SCIENCE CENTER
TEXAS, UNIVERSITY OF
TEXAS, UNIVERSITY OF ARLINGTON
TEXAS, UNIVERSITY OF EL PASO
TORONTO, UNIVERSITY OF
TUFTS UNIVERSITY
TULANE UNIVERSITY
U.S. DEPARTMENT OF AGRICULTURE
U.S. NAVAL ACADEMY
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
WRIGHT STATE UNIVERSITY
WYOMING, UNIVERSITY OF
YALE UNIVERSITY

DOE National Laboratories

AMES LABORATORY
ARGONNE NATIONAL LABORATORY
BROOKHAVEN NATIONAL LABORATORY
IDAHO NATIONAL LABORATORY
JEFFERSON LAB
LAWRENCE BERKELEY NATIONAL LAB
LAWRENCE LIVERMORE NATIONAL LAB
LOS ALAMOS NATIONAL LABORATORY
NATIONAL RENEWABLE ENERGY LABORATORY
OAK RIDGE NATIONAL LABORATORY
PACIFIC NORTHWEST NATIONAL LABORATORY
SANDIA NATIONAL LABS/ALBUQUERQUE
SANDIA NATIONAL LABS/LIVERMORE
SAVANNAH RIVER NATIONAL LABORATORY
SLAC NATIONAL ACCELERATOR LABORATORY

I. MATERIALS SCIENCES AND ENGINEERING DIVISION

Biomolecular Materials

Institutions Receiving Grants

Protein-Templated Synthesis and Assembly of Visible-Light-Driven Semiconductor Nano-Architectures for Efficient Hydrogen Production

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Sr. Investigator(s):	Prevelige, Peter, ALABAMA, UNIVERSITY OF
Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$220,000

This multidisciplinary proposal builds upon a strong scientific foundation and proven multidisciplinary teams for the development of protein-based templates that create novel photocatalytic materials through hierarchical assembly and molecular-level integration of light harvesting chromophores with semiconducting nanoparticles. Two teams, one at Montana State University (MSU) and one at the University of Alabama (UA), will pursue the biomimetic synthesis of materials with advanced light harvesting and catalytic properties. This DOE team has a proven track record of success in understanding protein supramolecular protein assembly and using these architectures for inorganic nanoparticle synthesis, as well as the development of active materials for solar energy conversion, and interrogation of the photophysical properties using ultrafast spectroscopy. The MSU team will focus on utilizing the interior of the P22 capsid for coordination polymer and semiconductor nanoparticle synthesis and characterizing the resulting materials via time-resolved spectroscopy. The UA team will emphasize the protein supramolecular assembly, synthesis of inorganic light harvesting materials using biomimetic methods on both the interior and exterior surfaces of P22, and evaluation of the photocatalytic activity of these materials. Both teams will take advantage of the unique symmetry-broken architecture available in P22 to produce Janus and Gemini particles with multiple nanoparticle components that can be brought into close proximity for light harvesting and photochemical reactivity. These parallel tracks capitalize on the demonstrated strengths of MSU and UA researchers and provide a broad spectrum of interdisciplinary expertise and experience that will be shared among the team members.

The biological world is an important inspiration and source of raw materials for nanomaterials fabrication. The high fidelity and specific activity of biological materials is made possible through hierarchical assembly of organic and inorganic components, mediated by molecular interactions that span the molecular to macroscopic length scales. From the nanomaterials point of view, a truly unique aspect of biological systems is that they are both active and responsive. The inspiration for the proposed “hard materials” research activity is derived from biomineralization where phase, crystallinity, morphology, and particle size determine material properties. Virology is the inspiration for the "soft materials.” Virus protein cage architectures provide the opportunity for the creation of multifunctional nanomaterials based on the inherent multi-valency, precise spatial arrangement of ligands, and the incorporation of catalytic activity on robust, high-symmetry viral architectures. Our understanding and control of these systems allows us to proceed well beyond the bounds of biology into purely synthetic systems that take advantage of the design, hierarchical ordering, and functionality characteristic of biological systems. In particular, the ability to template materials of different composition and to arrange them in a spatially defined manner is a hallmark of the proposed research. Together, the biological and synthetic approaches offer new opportunities for generating advanced materials that will play a transformational role in the development of materials with unique optical properties for light harvesting and photocatalytic applications.

The Specific Aims of this proposal are (1) direct encapsulation of materials on the interior of the P22 protein cage; (2) modification of the exterior surface of P22 protein cages; (3) use of alternative architectures based on symmetry broken P22 capsids, with portal complex, as templates; and (4) probing of the spectroscopic characteristics of P22 templated materials.

Success of this proposal is enhanced by the integration of the research teams through exchange of personnel, materials, results, and expertise between labs, developed over the last four years and a management structure that is top-down in resource allocation and research emphasis, but bottom-up in fostering and consolidating student and post-doc interactions between labs.

Engineering the Interface Between Inorganic Materials and Cells

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$185,000

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.

Dynamical Self-Assembly: Structure- Dynamics-Function Relations in Heterogeneous Phospholipid Membranes

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Sr. Investigator(s):	Sinha, Sunil, CALIFORNIA, UNIVERSITY OF SAN DIEGO
Students:	2 Postdoctoral Fellow(s), 3 Graduate(s), 2 Undergraduate(s)
Funding:	$327,000

The enormous compositional complexity of cellular lipidome naturally raises a fundamental question: How are membrane components organized? A simple application of Gibb’s phase rule (P= C-F+2, where P, C, and F represents number of independent phases, components, and variables respectively) predicts an unusually large number of co-existing independent phases within the equilibrated membrane medium. Experimentally, however, the number of co-existing phases in cellular membranes is almost invariably limited. A plausible hypothesis, in this regard, is that the membrane’s compositional heterogeneity is effectively reduced because many membrane components do not exist as chemically independent species and exhibit preferential associations forming structural (e.g., curvature-dependent) and compositional (e.g., micro-domains) complexes and assemblages. These compositional and structural biases, or organized heterogeneities in membranes, then couple with in-plane and out-of-plane dynamics (itself spanning a broad range of length- and time scales) to produce the array of spatially and temporally distinct membrane functionalities (e.g., molecular recognition, energy transduction, and transport). In this regards, it appears that the coupling of compositional heterogeneity and dynamics confers living systems a significant evolutionary advantage in placing function before structure.

From the vantage of materials science, such dynamic self-assembling systems – those that develop local temporal organizations to perform time-dependent tasks – offer a tremendous opportunity to devise entirely new classes of complex materials with dynamic properties. Over the past funding cycles, we have been developing model membrane configurations and characterization capabilities to abstract design principles of dynamic self-assemblies such as forms in synthetic, fluid lipid bilayers. We have now developed many classes of interface-templated membrane configurations and adapted many optical and fluorescence based techniques for characterization of their spatial and temporal dynamics over a range of length- and timescales. In particular, quantitative applications of fluorescence photobleach recovery, total internal reflection fluorescence, and time-resolved aqueous phase imaging ellipsometry provide diffraction-limited spatial resolutions. Smaller spatial resolutions are achieved by adapting X-ray photocorrelation spectroscopy, neutron spin-echo, and off-specular measurements spanning a broad range of time scales.

In the present proposal, we focus on three dominant classes of dynamic self-assemblies and their functional reorganizations within the membrane media. Specifically, we examine composition, curvature, and interface-templated dynamic organizations and their reorganizations following specific physical and biochemical stimuli. Specific complex systems chosen include (1) the studies of hierarchy of dynamic (and stimuli adjusted) organization of cholesterol-enriched nanoscale dynamic assemblies within lipid bilayers and (2) curvature-dependent localization of specific lipid-types such as in bacterial and plant photosynthetic membranes. Interplay of curvature, composition, interfacial hydration, and elastic properties of the membrane media afford a tight synergy between the specific aims.

Beyond membrane dynamics, we expect that these studies will contribute further, toward developing a general understanding of dynamic self-assembly mechanisms in broader classes of interfacial complex fluids. We also expect that these studies will allow for the abstraction of design rules toward the synthesis of useful biomimetic systems with designed synthetic and possibly biological functionality. This research profits from the co-PIs expertise in molecular self-assembly, membrane-mimetic chemistry, optical and vibrational spectroscopy and microscopy, and a suite of structural and dynamical characterization tools based on X-ray and neutron scattering based methods. The project provides dissertation opportunities for graduate students at the interface between physical and biological science with an emphasis on materials science. The proposal recognizes that advanced characterization of complex materials increasingly relies upon access to state-of-the-art characterization techniques such as at DOE national user facilities. The work offers our students opportunities to work with Advanced Photon Source at Argonne (APS), National Institute for Standards & Technology (NIST), Center for Integrated Nanotechnologies (CINT), and Los Alamos Neutron Scattering Center (LANSCE) via their user programs.

Biomimetic 3D Network Polymers Containing Reversibly Unfoldable Modules (RUM's) for Strong and Tough Materials

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

The goal of this project is to develop strong H-bonding-mediated self assembly of nanomaterials having adaptive and dynamic properties for energy relevant applications. Inspired by natural dynamic and adaptive materials, we propose to use strong, reversible H-bonding mediators to achieve dynamic assembly of nano-objects. The dynamic nature of hydrogen bond arrays are proposed to introduce adaptive, autonomically responsive, and self healing properties to the nanomaterials. Our progress in FY 2011 is briefly summarized below.

PROGRESS DURING FY 2011

First, we have succeeded in designing stiff and autonomous self-healing polymers that do not require any external stimuli, healing agents, or solvents/plasticizers. Our approach is to incorporate programmed dynamic interactions (H-bonds, etc.) into different polymer architectures to achieve self-assembled, multi-phase dynamic nanocomposites. The microstructure in bulk is analogous to that of conventional thermoplastic elastomers (TPEs) whose superior mechanical properties result from a self-assembled nanostructure consisting of stiff, glassy domains permanently connected by a flexible matrix. In our design, the covalent connections are replaced by dynamic supramolecular connections based on polyvalent dynamic interactions. Unlike covalent bonds, which rupture irreversibly due to highly reactive fracture intermediates, these dynamic connections can reform quantitatively after damage without external stimuli.

Second, for dynamic nano-assembly, we have successfully functionalized C60 with symmetrically spaced well-defined molecular recognition motifs. Assembly of nano-objects into better-defined 3-D structures is also of great importance for the “bottom-up” manufacturing of macroscopic materials from nano building blocks. C60 is interesting for constructing 3-D dynamic assemblies due to its well-defined nanostructure, excellent mechanical properties, and well-developed functionalization methodologies. We have synthesized UPy-functionalized C60, and observed their controlled self-assembly into ordered nanosheets. We have also successfully demonstrated the synthesis of hydrogen-bond-grafted silica nanoparticles, which self-assemble into mechanically robust, highly ordered bulk materials.

Bio-Inspired Routes for Synthesizing Efficient Nanoscale Platinum Electrocatalysts

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Sr. Investigator(s):	Wang, Joseph, CALIFORNIA, UNIVERSITY OF SAN DIEGO
Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$230,000

The overall objective of the proposed research is to use fundamental advances in bionanotechnology to design powerful platinum nanocrystal electrocatalysts for fuel cell applications. The new economically-viable, environmentally-friendly, bottom-up biochemical synthetic strategy will produce platinum nanocrystals with tailored size, shape, and crystal orientation, hence leading to a maximum electrochemical reactivity. There are five specific aims to the proposed bio-inspired strategy for synthesizing efficient electrocatalytic platinum nanocrystals: (1) isolate peptides that both selectively bind particular crystal faces of platinum and promote the nucleation and growth of particular nanocrystal morphologies, (2) pattern nanoscale 2-dimensional arrays of platinum nucleating peptides from DNA scaffolds, (3) investigate the combined use of substrate patterned peptides and soluble peptides on nanocrystal morphology and growth, (4) synthesize platinum crystals on planar and large-area carbon electrode supports, and (5) perform detailed characterization of the electrocatalytic behavior as a function of catalyst size, shape, and morphology.

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

Institution:	CALIFORNIA, UNIVERSITY OF SAN DIEGO
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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 3 Graduate(s), 3 Undergraduate(s)
Funding:	$200,000

GOALS

The goals of our 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 and (2) exploit the extensive non-covalent interactions formed around the interfacial metal sites within these protein frameworks to control the metal reactivity.

These goals combined will lead to the chemically controllable self-assembly of well-ordered superstructures under ambient conditions that will be used for light-harvesting and redox catalysis.

These structures also will provide a framework for a fundamental understanding of protein self-assembly as well as crystal nucleation and growth.

HIGHLIGHTS

Some highlights from the last funding period include the following:

We have our inorganic and protein design toolkits, with which we can better control the coordination chemistry of metal ions on protein surfaces and interfaces. This was achieved through the synthesis of various non-natural metal-chelates that can be appended to surface cysteine residues and through new protein design strategies.

One of the goals of our project is to internalize metal centers in completely unbiased/uniformed protein interfaces and design metal-based functions, particularly redox catalysis, from first principles. Using our approach of Metal-Templated Interface Redesign (MeTIR), we constructed a stable, tetrameric assembly of cytochrome cb562 monomers that were templated by tetrahedral Zn(II) coordination. The engineered hydrophobic interactions and disulfide bonds around the Zn templates resulted in an assembly that is one of the most stable protein complexes ever engineered (Kd ~ 50 nM), and binds Zn(II) more selectively over other divalent metal ions than any small molecule ligand platform. In its interfaces, this tetrameric scaffold can stably house Cu in +1 and +2 oxidation states as well as in a dinuclear arrangement, which is highly reminiscent of Cu-enzymes involved in dioxygen binding and activation.

Symmetrical, homooligomeric protein assemblies are highly prevalent in nature. For a major fraction of these proteins, their homooligomeric nature (and thus their shape) are intimately linked to their function. Using Metal-Directed Protein Self-Assembly, we were able to assemble cyt cb562 derivatives into open pentagonal or closed, tetrahedral architectures via directed Zn coordination, and thoroughly characterize their structures. We were further able to trap flexible and thus crystallographically unwieldy species (a heme microperoxidase) on the inside of the tetrahedral cage, which allowed its atomic structure to be resolved for the first time.

In the field of Supramolecular Coordination Chemistry, inorganic chemists have been particularly successful in exploiting the directionality and reversibility of metal coordination to construct stable 1-, 2- and 3-D coordination polymers through careful ligand design. Inspired by these efforts, we designed a dimeric cyt cb562 derivative (termed RIDC3) that presents a pair of three-coordinate Zn-binding sites, whose coordination vectors are orthogonally oriented. Using the Zn-RIDC3 dimer as a corner-like building block allows the Zn-dependent formation of uniform 1-D nanotubes (60 nm width, several microns long), and 2- and 3-D sheets (microns long/wide, nanometers thick) with crystalline order. The full structural characterization of these architectures through X-ray crystallography, transmission electron microscopy and cryo-electron microscopy has allowed a detailed structural understanding of how these various architectures form through Zn coordination and interconvert amongst themselves. This study, to our knowledge, represents the first example where a monomeric protein can be designed to yield (with 2-D constraints or templating) crystalline nanotubes and 2-D sheets.

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

The focus of the proposed research is to direct the assembly of single or binary nanoparticles into meso- or macroscale three-dimensional crystals of any desired configuration and crystallographic orientation without using prohibitively expensive lithographic processes. The epitaxial nucleation of defect-free, surface-bound bulk single crystals will revolutionize technologies for energy to generate new types of solar cells that yield maximum conversion efficiencies. It has been proposed that having a nanostructured bulk hetero-interface will enable efficient charge-carrier separations, similar to organic based heterojunction cells but with potential improvements, including thermal and long-term stability, tunability of energy levels, large adsorption coefficients, and carrier multiplication. However, engineering such devices requires nanoscale control and ordering in both two and three dimensions over macroscopic areas, and this has yet to be achieved. In nature, bulk organic and inorganic materials are arranged into precise and ordered programmed assemblies through the sequestration of raw materials into confined spaces and association through highly specific non-covalent interactions between biomolecules. Using similar strategies, the proposed research will focus on confining metal and semiconductor nanocrystals to pre-determined surface patterns and controlling their arrangement through tunable, orthogonal biomolecular binding. Once a perfect two-dimensional seed layer has been constructed, successive layers of single nanocrystals will be nucleated epitaxially with long-range order and tunable crystallographic orientations.

The proposed research exploits the ability of biomolecules to bind specific targets in a tunable, orthogonal, multivalent, and reversible manner to the arrangements of DNA-nanoparticle conjugates on chemically defined surfaces. Through careful balance of the attractive and repulsive forces between the particles, the array, and the outside surface, it is envisioned that single or mixed nanoparticles can be packed to adopt uniform crystal orientation in two and three dimensions from simple mixing and annealing of biomolecule-nanoparticle conjugates with biomolecule-stamped surfaces. To control the crystallographic alignment of each particle with its neighbors, the nanoparticles will be assembled using a mixture of non-covalent biomolecular interactions. To create solar cells in which layers of donor and acceptor nanocrystals that are not only oriented normal to the top and bottom electrodes but are also arranged in a checkerboard pattern, multicomponent nanocrystals (e.g., CdSe, CdTe) will be conjugated with biochemical linkers such that only interactions between the CdTe and CdSe promote particle packing within the array. The proposed research will (1) elucidate the role of single and binary cooperative particle-DNA interactions in influencing nanoparticle crystallographic orientation in two and three dimensions, (2) understand how confinement of nanoparticles on patterned arrays of biomolecules and modification of the surrounding substrate can nucleate long-range order over macroscopic areas via predefined grain boundaries, and (3) synthesize and characterize DNA conjugated semiconductor nanocrystals and assemble them into 2-D and 3-D binary superlattice arrays for photovoltaics.

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

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Funding:	$350,000

New materials are needed to radically transform the efficiencies of energy harnessing, transduction, storage, and delivery for military and civilian applications; yet the synthesis of advanced composites and multi-metallic semiconductors with nanostructures optimized for these functions remains poorly understood and even less well controlled. To help address this need, we developed a new, biologically inspired, low cost, low temperature method for the kinetically controlled catalytic synthesis of nanostructured materials optimized for energy applications. Specifically, we accomplished three major goals:

(1) We used our bio-inspired, kinetically controlled catalytic synthesis method to produce, optimize and characterize novel nanocrystalline tin-in-graphite and tin-in-carbon nanotubes composites that yield exceptionally high power, high energy and excellent cyclability as high-performance anodes in lithium ion batteries. We used this synthesis method to investigate the fundamental and still poorly understood mechanisms and structural consequences of the alloying and de-alloying of lithium ions into and out of the nanocrystals of tin (and silicon) that we grew catalytically in situ within the compliant, conductive matrixes to better understand the rate- and capacity-limiting factors governing the performance of these composites as high-capacity and high-power anodes in lithium ion batteries In related work, we used a kinetically controlled catalytic synthesis method to produce a high power, high voltage spinel-carbon nanotube nanocomposite cathode for lithium ion batteries.

(2) We used our kinetically controlled catalytic synthesis method to control the structures and properties of the layered cobalt hydroxides and related materials. We analyzed these structures at the atomic level at DOE synchrotron and neutron diffraction facilities, proving that we can use this synthesis method to predictively control the local ordering and the distribution of metal-coordination states to better understand and optimize the structural basis of their magnetic, photovoltaic and photomagnetic behavior (potentially offering a revolutionary approach for harnessing solar energy).

(3) We conducted further molecular and genetic analyses and engineering of Silicatein, the self-assembling, structure-directing, silica-synthesizing enzyme that we previously discovered and characterized, in order 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. We conducted genetically engineered, DNA-directed protein expression and enzymatic mineralization on polystyrene micro-beads in water-in-oil emulsions, yielding synthetic surrogates of biomineralizing cells that were screened by flow sorting, with light-scattering signals utilized to differentially sort the resulting mineralized composites. We demonstrated the utility of this platform by evolutionarily selecting new recombinant silicateins with specific structural and catalytic properties to make new semiconductors never made in living systems. Our demonstration of this bioengineering route to new materials introduced in vitro enzyme selection as a viable strategy for mimicking genetic evolution of materials as it occurs in nature.

The materials synthesis methods we are developing are low-cost, low temperature, and operate without the use of polluting chemicals. The near-term application of the results of these studies includes the improvement of batteries and related energy technologies. The broader impact of the proposed research includes a deeper fundamental understanding of the factors governing the control of synthesis, the assembly and performance of a wide range of semiconductors, and other valuable inorganic materials, in order to enable their more economical and more efficient use for energy technologies including energy harvesting, transduction, and storage.

Mechanistic Studies of Charge Injection from Metallic Electrodes into Organic Semiconductors Mediated by Ionic Functionalities

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Funding:	$300,000

During this fiscal year, we have established an understanding of the charge injection mechanism in multilayer polymer light emitting diodes (PLEDs), the effect of thermal annealing of cationic conjugated polyelectrolytes (CPEs) on the device performance, and surface reconstruction in conjugated oligoelectrolytes (COEs). Improving the device turn-on time by molecular design and processing conditions has been demonstrated.

Although the performance of PLEDs with CPE EILs/Al cathodes are comparable or even better than devices with Ba cathodes having no electron injection barrier, the devices can exhibit long turn-on times attributed to slow ion migration. Luminance response times in the order of seconds can be observed in PLEDs with CPE EILs thus hindering application in display technologies. Thus, it is important to tune the chemical structure of CPE EIL to facilitate ion migration, and hence, improve the luminance response time. This past year, we focused on the control of ion motion to improve the device response time by using CPE EILs with polyethyleneoxide (PEO) unit. An anionic CPE containing substituents derived from PEO was used as an EIL in PLEDs. To facilitate ion transport and accelerate the PLED response time, we first thermally annealed the device at temperatures above Tm, while applying a small bias and then cooled the device rapidly while still under an applied bias to “freeze” or “lock” the ions at the interfaces. Subsequent operation of the device shows much faster luminance temporal responses. The reversibility of these devices, important for long term applications, was also studied. The performance of devices with “locked” ions remained unchanged after one week, exhibiting similar luminance response times as the initial conditions. The faster luminance temporal response and stability open the possibility of using CPE injection layers not only in lighting applications but in display technologies as well.

The effect of thermal annealing on the performance of PLEDs with a cationic CPE was also investigated. We identified a thermal-induced process of chemical transformation that reduces the ionic component of CPEs. The loss of intrinsic charge and ionic properties results in dramatic shift of the turn-on voltage of the annealed devices. By pre-annealing and post-annealing experiments, we propose that the thickness of EILs influences the preferred operating mechanisms for electron injection in multilayer PLEDs. A mechanism where ion migration plays the major role appears to be dominant in thick EIL PLEDs, while the interfacial dipole model is the main effect in thin EIL PLEDs. These results are important for long term applications of PLEDs with CPE EILs in lighting and display technologies. Annealing must be avoided in these devices or CPEs with more stable functional groups should be used.

Miniaturized Hybrid Materials Inspired by Nature

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Funding:	$250,000

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 angstroms to micrometers.

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.

The cytoskeleton of neurons consists of a striking array of assembled bundles and networks of the structural proteins filamentous actin, microtubules (MT), and neurofilaments. The nature of the interactions leading to their hierarchical structures, and the structure-function correlations are, however, not understood. In earlier work, using a combination of synchrotron x-ray scattering, electron microscopy, and optical imaging, we discovered how MTs (highly charged nanotubes) are assembled in the presence of counter-ions, either in two-dimensional sheet-like bundles or in three-dimensional close-packed bundles through a competition between short-range attractions and long-range repulsions. Another one of our aims is to further elucidate in a reconstituted biological system, and to mimic, in a synthetic system, the rules of higher-order-assembly resulting from a competition between long-range repulsion and short-range attraction. The proposed systems include microtubule-associated-protein (MAP)-tau directed assembly of MTs. Variations in the six wild-type MAP-tau isoforms leading to changes in the interactions between MAP-tau coated MTs with tunable long-range repulsion and short-range attraction, are expected to clarify the contributions of distinct interactions in the formation of different structures. Such an understanding will allow us to develop more robust biomimetic versions of directed higher-ordered-structures.

The projects utilize the broad spectrum of expertise of the PI and senior investigators in biomolecular self-assembling methods, synchrotron x-ray scattering, electron and optical microscopy characterization techniques, the application of the small-angle x-ray scattering (SAXS)-osmotic pressure technique for direct force measurements, and custom organic/polymer synthesis and purification of biological molecules. The results of the research should aid in the development of nanoscale biomimetic materials with potential applications including templates for nanostructures (e.g., building blocks for hierarchical nanomaterials, nanowires, tips, needles), chemical encapsulation systems, and biosensors.

RNA Mediated Synthesis of Catalysts for Hydrogen Production and Oxidation

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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.

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

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We propose to synergistically combine theory and experiments to understand the stability and activity of immobilized enzymes on supports of different curvature with the goal of optimizing their stability and activity.

In specific examples of applied biotransformation, enzymes immobilized on/in solid/porous supports offer potential advantages over their use free in solution or in whole-cell expression systems. Enzyme immobilization has been a topic of study for decades, although only recently have these efforts focused more on understanding and improving enzyme performance at the support surface and influencing enzyme function. Previous research has led to the observation that surface curvature and chemistry are important, perhaps as they relate to protein-protein interactions at the surface, to protein-surface interactions, and in addition to intrinsic protein stability. The ability to control nm-level surface properties and the availability of different surface chemistries provide motivation to study the effect of these parameters on enzyme function in more detail. Different surface curvatures and enzyme packing densities will be studied, and enzymes will be adsorbed to the surface or covalently tethered. Finally, the arrangement of two different enzymes catalyzing a series reaction (conversion of 2-keto-isovalerate to isobutanol) will be studied to better understand how various spatial criteria influence the series reaction. A variety of theoretical and computational tools will be intimately connected and used to develop models that capture relationships between surface properties and protein thermodynamics (e.g., to understand the role of curvature on unfolding).

Rationale: Short life-time and low power density are major limitations to a successful, competitive enzyme-based biofuel cell. Low volume capacity and slow reaction kinetics with feed-back inhibition could inhibit the economic production of high-carbon number alcohols using modern genetics in microbes in conjunction with fermentation. For both these applications, bio-catalyst or enzyme stability critically determines performance. While this topic is thus of broad-based interest in the context of alternative fuels, for the sake of focus, we limit our attention in this proposal to the production of biofuels. While the enzymatic production of biofuels is typically conducted via fermentation with bacteria (e.g., E. coli.), or more recently with yeast, it has been argued that much more efficient methods can be devised in a cell-free environment. It has been suggested that many of the limitations associated with the use of enzymes in free solution (e.g., low productivity and low stability) could be overcome by immobilizing them. Germane examples of success using this strategy are in sensors, in bio-fuel cells, in large scale industrial use (amino acid production, separation of racemates), and in household applications for cleaning and food applications.

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

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Funding:	$300,000

Progress has been made in all aspects of the project. Regarding in vivo enzyme immobilization, we have focused on (a) investigating the scope of the LiDSI method for enzymes that require oligomerization, cofactors, and posttranslational modifications for activity, and (b) identifying and functionally analyzing a targeting signal for intracellular delivery of proteins to the SDV (i.e., the silica-forming organelle). Regarding in vitro enzyme immobilization, our efforts have been directed towards (c) understanding the mechanism(s) of BASIC conversion and (d) developing methods to generate high surface area C and Au replicas for subsequent attachment of energy-relevant enzyme glucose oxidase (GOx).

Hyperbranched Conjugated Polymers and Their Nanodot Composites as Universal Bioinspired Architectures

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Funding:	$218,000

We will systematically investigate the electronic interactions between gold nanoparticles, (ANP) and conjugated materials of the poly¬(phenyleneethynylene) (PE) type to obtain a road map for the successful "hardwiring" ANPs to conjugated polymers. We will investigate the interaction by the ability of the ANPs to quench the fluorescence of both linear and hyperbranched PEs.

(1) The synthesis of hyperbranched conjugated polymers (HCP) of the PE type is proposed. These bioinspired and biomimetic polymers should provide valuable scaffolds that will allow efficient volume/volume connection to probe the interactions of peripheral clients such as ligands for the ANPs with the fluorescent/chromic HCP scaffold for efficient signal transduction and resonance energy distribution.

The synthetic scheme is based upon the Pd-catalyzed monoalkynylation and further elaboration of unsymmetrical 1,2,4-triiodobenzene derivatives that carry an additional solubilizing auxiliary group in the 3-position. The Pd-catalyzed polymerization of these y-shaped monoalkynyl-diiodo-monomers will lead to HCPs that have an equal number of aromatic iodide end groups the number to the degree of polymerization. This approach will furnish a universal backbone to be elaborated further by the coupling to functionalized aromatic alkynes that contain amino, thiol, cyano, isocyanato, nitro, etc. substituents.

(2) We will equip the HCPs with suitable mannose and sialic acid substituents and explore their multivalent binding towards bacteria, proteins and toxin models as a continuation of our program dealing with bio-inspired conjugated polymers. We expect exceptionally high binding constants between the now densely-functionalized mannosylated HCP and the bacterial or protein-based sugar glyco-receptors as these HCPs support three dimensional multivalent interactions between the sugar moieties and their receptors.

(3) We will investigate the complexation of differently end capped HCPs, side-chain functionalized linear CPs, and small molecule ligands with ANPs of different size. Through this semi-systematic three-pronged approach we hope to establish a simple "periodic table" of NP/chromophore interactions and identify magic combinations of size, ligand and scaffold architecture in which the electronic interaction between chromophore and NP are maximized/optimized. The interactions will be probed by optical and electronic spectroscopy in thin films and in solution as well as by conductivity measurements and Stern-Volmer quenching. This approach will guide the synthesis of NP-based CP hybrids. Such materials are expected to display superior performance in photovoltaic cells and in light emitting diodes and tunnel diodes.

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

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The goal of this project is to develop materials, strategies, and architectures for hybrid nano/microstructured surfaces which sense and autonomously respond to a changing environment. We undertake a bio-inspired approach to the design of such systems by combining the unique properties of nanoscale structures with the responsive behavior of hydrogels in order to create hybrid surfaces with tunable and dynamic properties; we have termed such surfaces hydrogel-actuated integrated responsive systems (HAIRS).

HYDROGEL-ACTUATED POLYMER MICROSTRUCTURES OPERATING IN RESPONSE TO pH

To generate HAIRS applicable in fluidic environments, we integrated a pH-responsive poly(acrylic acid-co-acrylamide) hydrogel with polymeric high-aspect-ratio microstructured surfaces. We studied the actuation kinetics as well as demonstrated actuation of asymmetric fin-shaped structures which, due to their preferential bending direction, allow for the fabrication of large areas (cm^2) of highly uniform actuation. Additionally we have demonstrated actuation these microfin HAIRS with microfluidic channels.

CONTROLLING THE STABILITY AND REVERSIBILITY OF MICROPILLAR ASSEMBLY BY SURFACE CHEMISTRY

Instead of using hydrogels as the force for structure actuation, we used capillary forces to drive their initial self assembly, and we examined how the surface chemistry of the structures affects the stability and reversibility of clustering as well as their adhesion in different solvents.

STRUCTURAL TRANSFORMATION BY ELECTRODEPOSITION ON PATTERNED SUBSTRATES (STEPS)

Polypyrrole was electrochemically grown to user-defined thicknesses on gold electrodes patterned in various ways on original epoxy nano/microstructures. STEPS therefore allows us to systematically vary geometric characteristics of our structures that we use for HAIRS quickly and cheaply therefore letting us experiment with a wide range of geometries that would have otherwise been prohibitively expensive and time consuming to produce by traditional fabrication techniques.

DIRECT WRITING AND ACTUATION OF 3D-PATTERNED HYDROGEL PADS ON MICROPILLAR SUPPORTS

We have developed methods for patterning pH-responsive and temperature-responsive hydrogels in three dimensions with microscale precision using multiphoton lithography. Hydrogels of only a few microns in thickness are tethered near the tips of microstructures and therefore the gels are left relatively unconstrained and retain large swelling ratios necessary for actuation. We also demonstrated that multiple kinds of gels can be patterned in sequence with precise registration of materials; we are now able to affect actuation of structures using two "muscles" meaning that surfaces can now respond to multiple combinations of independent stimuli.

FUTURE PLANS

We are currently exploring the use of temperature-responsive hydrogel to create surfaces with unique responsive optical and thermal properties. By metal-coating the sides of the microstructures, we are able to create surfaces showing reversible reflection and transmission properties. Additionally, we are continuing to investigate the use of HAIRS within microfluidic environments. Specifically, we aim to create a responsive system capable of a feedback mechanism which controls a chemical reaction in situ. We also are exploring the use of the HAIRS as anti-fouling surfaces and prevention of biofilm growth. Other stimuli, including light, redox states, and biological molecules are also of interest.

Dynamic Self-Assembly, Emergence, and Complexity

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Funding:	$200,000

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.

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.

SIGNIFICANCE

(1) It is clarifying the characteristics of complexity: that is, the relations between interactions and properties in physical (e.g., not theoretical or computer-based) systems that are tractably simple (relatively small numbers of simple components) but still show emergent behaviors.

(2) It has proved successful in generating new phenomena and materials that can be developed to understand materials, and to solve problems in chemical, materials, and biological science. Examples include systems of bubbles in microchannels, electrets and electrostatically charged matter, flames, and others.

(3) It is developing physical systems that can provide tests of theory in fields such as self-assembly: “electrostatic matter” based on electrets is the most advanced of these systems.

(4) It is focusing attention on dissipative and out-of-equilibrium systems. Much of science is based on the study of systems at equilibrium or at steady state, but many of the most interesting phenomena in nature are dissipative. This work is contributing to building an intellectual bridge between the two.

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

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We have developed a robust methodology for investigating a wide range of properties of phospho-lipid bilayers. The approach developed is unique because despite using periodic boundary conditions, we can simulate an entire experiment or process in detail. For example, we can follow the entire permeation process in a lipid-membrane. This includes transport from the bulk aqueous phase to the lipid surface, permeation into the lipid, transport inside the lipid, and transport out of the lipid to the bulk aqueous phase again. We studied the transport of small gases in both the lipid itself and in model protein channels. In addition, we have examined the transport of nanocrystals through the lipid membrane, with the main goal of understanding the mechanical behavior of lipids under stress. Finally we have also examined in detail the deformation of lipids when under the influence of external fields, both mechanical and electrostatic (currently in progress).

We have also carried out some related fundamental level studies on the flow of polar fluids like water in nanochannels to understand the molecular principles that govern such flow. More details are given in our published reports. Our results have shown some rather interesting behavior. We have looked at both the effect of surface characteristics (hydrophobic or hydrophilic) and channel geometry on such flow. Our results have shown, for example, that free (capillary) flow is enhanced if the surface is hydrophilic and closely follows Young’s equation. On the other hand, forced (pressure driven accomplished by compressing the fluid to force it into the channel) flow is higher if the surface is hydrophobic. This is because a hydrophobic surface minimizes the interaction between water and the surface, which results in almost frictionless flow, while hydrophilic surfaces can offer significant resistance to flow in nanochannels.

Structure, Stabilized Phospholipid Vesicles

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Funding:	$229,000

This proposal has the objective to develop the science basis needed to deploy phospholipid bilayers as functional materials in energy contexts. Specifically, in the presence of nanoparticles and other adsorbates, we aim to (1) develop an integrated molecular-level understanding of what determines their dynamical shape, phase behavior, and spatial organization 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. The methods to do this largely involve fluorescence imaging and other types of fluorescence spectroscopy involved single particles and nanoparticles, vesicles, and liposomes. Some of the specific objectives of this renewal proposal are the logical next step of research on which this laboratory embarked 2 ½ years ago. Others are fundamentally new. While fundamental understanding is the main goal, integrated understanding will be useful for rational design of biologically-inspired materials function, as the proposed experiments are generic in scope.

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

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Pi-conjugated organic materials are the subject of intense research on account of their strong prospects to revolutionize efficient lighting and energy generation with materials castable over large areas, flexible electronics for sensor applications, lightweight materials for energy storage, and nanoscale electronic materials that mimic biological function and interface with living cells. The efforts described here will focus on our group's established interests in the control of intermolecular interactions dictated by peptide-based self-assembly schemes. In the present research plan, we will develop a broad-array of biologically relevant pi-electron materials capable of self-assembly into well-defined one-dimensional nanostructures. We emphasize throughout the prospects for meeting several DOE priority needs in regards to (1) exploratory synthesis and understanding of new forms of matter, (2) the development of biologically-inspired hierarchical materials with capabilities to bridge the biotic-abiotic interface, and (3) the interdisciplinary training of students fluent in soft materials-related energy research.

We previously reported the self-assembly properties of a unique class of biomolecules consisting of pi-conjugated oligomers embedded directly in the backbones of peptide chains. Self-association resulted in well-defined one-dimensional nanostructures with delocalized electronic properties arising from intermolecular pi-stacking among the embedded oligomers. We will advance our work towards this goal in the following specific tasks: (1) the synthesis of new pi-electron units to embed within self assembling peptides, (2) the detailed characterization of the internal structure of the aggregates necessary for energy transport using appropriate spectroscopies and optoelectronic measurements, and (3) the exploration of the surface chemistry presented by these nanostructures as relevant for inorganic semiconductor synthesis or for interfacing with membrane-bound cell surface proteins. We will use specific peptide sequences (a) as nucleation sites for metal or semiconductor nanoparticles that will encourage exciton dissociation from mobile carriers within internal pi-stacked regions and (b) to encourage the adhesion of integral membrane proteins as a first step to using these materials to interface with living cells.

Designing Two-Level Biomimetic Fibrillar Interfaces

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Funding: $285,000

Our aims are to fabricate, study, and model bio-inspired architectures for controlled surface mechanical properties such as adhesion, friction, and surface compliance. The focus of our current work is on:

- Active control of adhesion and friction by designing a mechanically bistable surface based on a film-terminated architecture. This surface can be switched repeatedly between an adhesive/high friction and non-adhesive/low friction state.
- Adhesion Selectivity in Surfaces by (a) shape, and (b) electrostatic complementarity. We have demonstrated selectivity by shape complementarity using rippled and channel/pillar surface architectures. We have also shown theoretically how surfaces with stripes of charge can lead to highly selectivity of adhesion.

High Efficiency Biomimetic Organic Solar Cells

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Funding: $275,000

Unlike conventional solar cell materials, organic semiconductors generate localized excitons when they absorb light. But 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. The donor-acceptor interface solves this problem by dissociating excitons into a hole in the donor and an electron in the acceptor. The driving force for the reaction can be controlled by tuning the energy levels of the donor and the acceptor.

Recently, however, it has been recognized that the combination of the hole and electron at the donor-acceptor interface also forms a bound charge transfer (CT) state. Although smaller than the binding energy of an exciton, the CT binding energy is still likely much greater than the thermal energy (~ 0.1 eV). The binding energy of a CT state opposes the generation of free charge, and encourages an important loss process – the recombination of the CT state into a neutral ground state. Thus, organic solar cells must overcome the binding energy of both the exciton and the CT state.

In this proposal, we address two key questions:

(1) How do excitons and CT states dissociate in organic solar cells?

(2) Will a biomimetic architecture help overcome the CT state binding energy? The biomimetic approach draws upon photosynthesis. In photosynthetic reaction centers, exciton dissociation is achieved through a multi-step electron transfer rather than a single donor-acceptor junction. A multi-step electron transfer can destabilize the CT states and rapidly separate the charge carriers. Indeed, the quantum efficiency of reaction centers is believed to exceed 95%.

Self Assembly & Self-Repair of Novel Photosynthetic Reaction Center/Single Walled Carbon Nanotube Complexes for Solar Energy Conversion

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Plants have evolved highly sophisticated self-repair mechanisms that allow them to adapt and regenerate under otherwise dire conditions. These self-repair processes enable plants to not only adapt in a manner that minimizes damage, but also fully recover from a state of excessive protein denaturation. Without these self-repair processes, plants would produce less than 5% of their typical photosynthetic yields with lifetimes on the order of minutes under intense illumination.

The focus of this project is to incorporate these natural mechanisms of self-repair into biomimetic, light-harvesting devices capable of autonomous and continual regeneration. Thusfar, we have developed the first synthetic photoelectrochemical complex capable of mimicking key aspects of the plant self-repair process. Under an illumination of 785 nm, this complex demonstrates a 40% per complex efficiency. Utilization of a biomimetic regeneration cycle has been shown to increase efficiency by over 300% over 168 hours of illumination and prolong solar cell lifetime indefinitely.

Our most recent efforts have focused on extending this platform to study the effects of nano-particle addition for plant-based regeneration. Specifically, we are developing and examining the preventative role of nanoparticulate-based radical oxygen scavengers in protein photodamage. The ability to incorporate such regeneration mechanisms into synthetic devices would allow for the development of low-cost biofuel cells with enhanced stabilities and indefinite lifetimes.

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

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Funding:	$200,000

The purpose of this project is to demonstrate the applicability of cholesterol helical ribbons for measuring forces between biological objects and for mapping the strain fields in hydrogels under stress. To achieve the objectives of the project as specified above, the following experiments will be performed.

For objective (1), we shall prepare cholesterol helical ribbons coated with a uniform layer of polydopamine. This coating is amenable to further modification. In particular we will explore metal plating as a means of stabilizing these ribbons within and outside of an aqueous solution. The properties of these coatings will be characterized using atomic force microscopy and by X-ray photoelectron spectroscopy. The spring constants of the modified helical ribbons will be measured using nanofabricated silicon-nitride cantilevers. By achieving objective (1), we will produce robust helical ribbons which can be readily tethered to various objects.

To achieve objective (2), we will prepare hydrogels containing embedded helical ribbons. We will measure the strain distribution within a stressed hydrogel by observing the changes in pitch angle of embedded helical ribbons. Specifically we shall investigate elastic and plastic deformation as well as the swelling of collagen gels. These properties of collagen gels are important in physiology and tissue engineering.

For objective (3), we will tether one end of the helical ribbon spring to a stationary post, and the other end to a functionalized polystyrene bead. The force exerted on the bead can be determined directly from the deformation of the spring. The utility of this micro-device will be tested in two sets of experiments. First we shall functionalize the bead with streptavidin. We will then measure the force required to detach the bead from a biotin activated surface. Second, we will functionalize the polystyrene bead with Act-A, the protein which facilitates actin polymerization. We will then measure the force produced by actin fibers growing next to the bead surface.

Our project underpins several energy-related areas. One key element of our project is to develop tools for measuring force between biological molecules. Forces generated in biological systems are associated with energy transfers. Thus, our tools will be useful in investigation of the energy transfer processes in biological systems. Another key objective of our proposal is to develop a method for monitoring stress and strain in biologically compatible matrixes (hydro-gels). There is great merit in exploring biocompatible matrixes capable to accommodate biomolecules with desired catalytic functions such as light-harvesting. In large-scale, industrial implementation of such “living” materials, the stress and strain generated in them become essential. It is thus clear that our project is fully compatible with the mission of MSE Biomolecular Material Research Area.

Simulation of Self-Assembly of Tethered Nanoparticle Shape Amphiphiles

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

Recently we used computer simulation and free energy calculations to demonstrate a simple design heuristic for assembling quasicrystals and approximants in soft matter systems. The surprising recent discoveries of quasicrystals and their approximants in soft matter systems poses the intriguing possibility that these structures can be realized in a broad range of nano- and micro-scale assemblies. It has been theorized that soft matter quasicrystals and approximants are largely entropically stabilized, but the thermodynamic mechanism underlying their formation remains elusive. Previously we reported on simulation studies of the self-assembly of dodecagonal quasicrystals and approximants in minimal systems of spherical particles with complex, highly specific interaction potentials. We can now demonstrate an alternative entropy-based approach for assembling dodecagonal quasicrystals and approximants based solely on particle functionalization and shape, thereby recasting the interaction-potential-based assembly strategy in terms of simpler-to-achieve bonded and excluded-volume interactions.

Spherical building blocks were functionalized with mobile surface entities to encourage the formation of structures with low surface contact area, including non-close-packed and polytetrahedral structures. The building blocks also possess shape polydispersity, where a subset of the building blocks deviates from the ideal spherical shape, discouraging the formation of close-packed crystals. Our results show that three different model systems with both of these features – mobile surface entities and shape polydispersity – consistently assemble quasicrystals and/or approximants. We theorize that this design strategy can be widely exploited to assemble quasicrystals and approximants on the nano- and micro-scales. In addition, our results further elucidate the formation of soft matter quasicrystals in experiment.

Protein Architectures for Photo-Catalytic Hydrogen Production

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Virus capsids are remarkably homogeneous in size, can be produced in large quantities, and are amenable to selective deposition of organic or inorganic materials (by design) at specific locations on the protein cage. This affords precise control over the size, spacing, and assembly of nanomaterials, resulting in uniform and reproducible nano-architectures. This multidisciplinary effort is aimed towards the development of a biomimetic approach to materials synthesis utilizing the bacteriophage P22 for coupled light harvesting and catalysis.

(1) PROGRAMMED CO-ASSEMBLY AND ENCAPSULATION USING THE P22 PROTEIN CAGE

The bacteriophage P22 assembles with the assistance of a scaffold protein (SP) into a T = 7 60 nm icosahedral shell with a 50 nm central cavity. Only the C terminal region of the SP is necessary for capsid assembly while the N-terminus can be truncated or fused to other proteins or polypeptides, with no effect on assembly. We have demonstrated the fusion of two different protein and polypeptides to the SP and demonstrated assembly of the P22 and encapsulation of the fusion product. The fusion of green fluorescent protein and a red fluorescent protein (mCherry) to the SP results in assembly of the P22 capsid with the GFP or mCherry encapsulated on the inside. Co-encapsulation of a triple fusion SP-GFP-mCherry (with a variable length peptide linker between the two fluorescent proteins) results in very efficient energy transfer when forced into the crowded environment of the capsid but complete loss of FRET when these are released from the capsid. This clearly demonstrates the effects of molecular crowding on the properties of the encapsulated cargo.

(2) TEMPLATED SYNTHESIS OF POLYMERS WITHIN PROTEIN CAGE ARCHITECTURES

When initiated inside the P22 capsid hyper-branched polymers structures can be grown from the walls of the capsid. We have incorporated metal coordination complexes into the polymer resulting in control over metal adjacencies and a high degree of polymer crosslinking. Initial photophysical studies of the light harvesting Ru(II) phenanthroline complexes as well as small molecule mimics of the polymer, incorporating both Ru(II) and Co(II) centers, are underway.

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

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Interfacing nanostructured and living systems are compatible at both the dimensional and energetic level. Electrochemical processes in living cell and nanostructures are both, in principle, sensitive to modulations by single electron. However, in aqueous media with ions, compartmentalizing local charging by single electron and transport remains a challenge in physical systems. This year, we made the following progress with respect to the above goal of developing and characterizing a physical system operating in aqueous media that can interface with living cells.

(a) A novel architecture composed of network of one dimensional nanoparticle was designed, developed, and studied. The network demonstrated single electron effect.

(b) Bio-gating in air was achieved. Microorganism Pichia pistoris was interfaced in air to demonstrate bio gating.

(c) A packaging scheme was developed to operate the nanoparticle necklace in aqueous media.

(d) A single electron device operating in aqueous media was demonstrated. A special optical method was developed to study the Fermi level and potential of zero charge of the network in aqueous media to understand the single electron effect. This, to our knowledge, is the first demonstration of single electron gating in aqueous media.

(e) Preliminary results indicate it is possible to electrochemically couple the network to E. coli in aqueous media.

Material Lessons of Biology: Structure-Function Studies of Protein Sequences Involved in Inorganic-Organic Composite Material Formation

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Although extensive development has been witnessed in the molecular biomaterials field, much of this development is empirical in nature (i.e., methods for material synthesis and molecular assembly are tested and found to work), but very little understanding emerges about how they work. This means we are limited in our ability to improve upon these methods or tweak them for other purposes. In other words, we can make things using biomimetic principles, but our comprehension of why they work or how to make them work better is lacking.

The main strength of our group is that we are investigating how Nature uses proteins to build inorganic-organic composites and control the nucleation of these composites. Our work is basic science in nature and we have developed a number of paradigms which describe the biological process of polymorph selection and composite formation within the mollusk shell. This information will speed the development of new methods in materials construction.

Room-Temperature Synthesis of Semiconductor Nanowires by Templating Collagen Triple Helices and Their Precise Assembly Into Electrical Circuits by Bio

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Funding:	$230,000

The ability to control self-assembly of complex 3D architectures from functional building blocks could allow further development of complex device configurations. This year we developed peptide-based assembly technology enabling the precise 3D superlattice assembly of metal nanoparticles. We did this in defined 3D shapes in unusual larger scale (from μm^3 to mm^3), with higher yield, and with higher reproducibility. In this work, nanoscale collagen peptides and ligand-functionalized gold nanoparticle joints were self-assembled into micron scale 3D cube-shaped crystals, creating a physical framework for the proposed biomimetic assembly strategy. Due to the design of amino acid sequence, this 3D superstructure can be reconfigured into other shapes triggered by pH change. Peptide assemblies that program the growth of the specific type of metal were also applied to biomimetic materials synthesis (PbSe) and sensor (heavy metal detection). The metal-coated peptide assembly showed interesting electron transport property and this mechanism was analyzed through various electric measurements.

Electrostatic Driven Self-Assembly Design of Functional Nanostructures

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Nature utilizes charged molecules to self-assemble its components. In particular, crystalline shells made of protein with various charged groups, including organelles, viral capsids, and halophilic organism wall envelopes, adopt various regular and irregular polyhedral shapes to compartmentalize matter in unknown ways. The envelope of halophilic microorganisms, for example, takes a square geometry in natural brines though the cell wall is actually composed of a hexagonal lattice. Self-assembled, strong, and salt-stable shells are essential for the development of technological processes, such as targeted delivery of materials into cells. We have developed a sophisticated multipurpose Monte Carlo code which allows us to rapidly generate and analyze shapes and patterns of multicomponent elastic shells that arise as a result of the self-assembly of ionic amphipiles with different charge ratios. The shells are assumed to consist of a thin solid membrane. Thus, next to the consideration of the bending contributions to the free energy, a proper description of these quasi two-dimensional systems requires introduction of the elastic terms that penalize stretching. The coupling between bending and stretching necessarily present in the spherical topology leads to a rich set of phenomena even in our minimal coarse-grained model. Our Monte Carlo code has elucidated the gallery of shapes of a two-component elastic shell assembled of two elastic materials with substantially different elastic properties, like bending rigidity and Young’s modulus, i.e., one component is set to be very stiff and therefore hard to bend, while the other is soft and easily accommodates large deformations. Such soft regions are believed to naturally arise at the contacts of the crystalline domains present on the surface of an ionic vesicle. In contrast to similar techniques used in the literature to study optimal shapes of various elastic sheets and shells, our approach makes no assumptions on either shape or component distribution, but uses a simulated annealing method to concomitantly optimize the shape and the distribution of the components.

The observed buckling mechanism is very different than the commonly reported icosahedral deformation located at the twelve topological disclination defects responsible for the transition from a spherical shape for small shell radii to an icosahedron for larger shells (e.g., as observed when studying shapes of various viruses). In the case of a two-component system, there is a separate pathway for the shell to relieve some of its stress. Instead of buckling at the effects, such shell can form very sharp ridges of the soft component. Those ridges are substantially bent with most of the curvature concentrated along them. As a result, nearly flat facets of the hard component are formed and the shell takes a polyhedral shape. The exact number of facets as well as the optimal shell shape is determined by the relative fraction of the two components and the ratio of their elastic constants. It is worth noting that while vast majority of obtained shapes are irregular with a carefully tuned set of elastic parameters and component fractions, one can obtain regular Platonic and Archimedean solids.

Despite a very rich variety of observed polyhedral shapes, including highly symmetric Platonic structures, the model described does not include energy penalty for mixing of the components, i.e., no line tension is associated with the boundary between the soft and hard domains. As such domains in principle can arise by mixing chemically different amphiphiles, it is natural to expect a certain degree of mixing penalty. In an expansion or our model, it is extended to include line tension between soft and hard components. The gallery of the resulting optimal shapes is even richer than with no line tension, with various polyhedral and Janus-like shell structures.

In addition to the crystallization of the lipid molecules for very small shells (diameter ~20nm), the electrostatic interaction can lead to a reversible collapse of the structure. Our work has shown that for weak electrostatic interactions, the elastic energy wins and electrostatics only slightly perturb the shell shape. As the strength of the electrostatic interaction is increased (e.g., by tuning pH or the salt concentration of the surroundings), the shell can undergo a full collapse. We have also recently generated a large variety of shell geometries, either fully faceted polyhedral or mixed Janus-like vesicles with faceted and curved domains that resemble cellular shells by co-assembling a water-insoluble anionic (–1) amphiphile with cationic (+2 and +3) amphiphiles. Our electron microscopy, x-ray scattering, theory, and simulations works demonstrate that the resulting faceted ionic shells are crystalline and that they are stable at high salt concentrations. Elastic inhomogeneities resulting from the competition of ionic correlations with charge-regulation explain the unusual shapes. This work promotes the design of faceted shells for various applications and improves our understanding of the origin of polyhedral shells other than icosahedra in nature.

Nanoengineering of Complex Materials

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This ongoing research program has been focused on the development of supramolecular self-assembly strategies to create soft materials and their hybrids with inorganic phases. We are particularly interested in biomimetic pathways that lead to complex materials with hierarchical organization of nanoscale components across scales. The functions guiding the materials design include the transduction of energy, catalytic activity, environmental stability of materials, and biomolecular structures that can interact with biological systems. Over the past funding period we discovered the first example of reversible x-ray induced crystallization using charged filamentous assemblies of small molecules. We also investigated further self-assembly between small molecules and oppositely charged macromolecules. This work included the formation in these systems of complex structures with external fields, and microscopic structures that resemble cells. Other important achievements include a pathway that improves the macroscopic orientation required in photovoltaics of hybrid lamellar materials, and organic systems designed molecularly for an n-type component to bind into cavities of p-type organic assemblies in order to optimize exciton splitting.

We propose here a research plan on three topics: (1) self-assembly of hierarchically organized structures formed by small molecules alone or in some systems macromolecules as well, (2) organic-inorganic hybrid lamellae, and (3) artificial environments to host bacteria. In the self-assembly section, we describe dynamic self-assembly of large and small molecules into closed structures to create cell-like objects, filamentous crystals, or open membranes. The targeted structures of the proposed plan were selected to investigate catalytic microstructures, model systems to harvest solar energy, or synthesis of new materials. In the second area, we investigate pathways to organize p-type and n-type semiconducting lamellae on macroscopic scales, which is a critical structural feature in photovoltaic cells; we also investigate chemistry within these systems that could be useful for energy storage. The third part of the research plan proposes to investigate the recently discovered aqueous monodomain gels with orientational order on macroscopic scales to host bacteria and explore the possibility of changing their behaviors with features of the external environment. These recently developed monodomain gels can direct cell migration and diffusion of molecules and offer the opportunity to study chemical signaling among bacterial populations.

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

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This project is proposed to, at a molecular level, understand and effectively control the dynamics of charged and neutral molecules at polyelectrolyte (PE) brush surfaces of tunable chain nanostructures and interfacial interactions under external stimuli. Specifically, the PI aims to quantify and optimize the conformational nanostructures of PE brushes to consequently enhance interfacial molecular dynamics under varied solution pH, added salts and applied ac-electric fields. The objectives of this proposal include (1) investigating the coupling of brush conformations and local counterion concentration of PE brushes of varied grafting density and thickness in response to solution pH and added salts; (2) examining the interfacial dynamics of single probe molecules, neutral versus charged, on weak PE brush surfaces; and (3) actively tuning the conformational dynamics of weak PE brushes by nanoscaled ac-electric manipulation to effectively enhance interfacial ion and molecular transport. 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, respectively.

The uniqueness and novelty of this research relies on single-molecule characterization with in-situ ionic and ac-electric manipulations to actively modify the nanostructures of PE brushes and thereby effectively control interfacial molecular dynamics. The detailed molecular information obtained from this endeavor, unavailable from coarse-grained simulation modeling and ensemble-averaged characterization, makes this project a distinct contribution to the research on developing “smart” or adaptive materials and surface coatings. A new paradigm in molecular design of PE based multi-responsive polymer thin films with tunable interfacial nanostructures will be established to effectively control interfacial interactions as well as interfacial energy and molecular transport. Hence, the knowledge gained from this endeavor can be employed by DOE to design and synthesize novel functional materials for broad energy-related applications ranging from polyelectrolyte multilayer assemblies as energy storage membranes, lubricious and fouling preventive coatings, to biomimetic and adaptive materials synthesis for controlled chemical release and energy conversion. When combined with current microfluidics technology, nanoscaled ac-electric manipulation of PE brushes can be developed as a novel and viable approach for constructing switchable engineering surfaces as well as controlling specific molecular recognition.

A Hybrid Biological/Organic Half-Cell for Generating Dihydrogen

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The goal of our BES-funded program in Materials Science and Engineering 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. The strategy to achieve this goal is to employ a technology based on directly connecting surface-located redox centers with a molecular wire, which serves to tether the photochemical module to the catalytic module at a fixed distance so that an electron can quantum mechanically tunnel between the F_B cluster of PSI and the distal [4Fe-4S] cluster of a H_2ase enzyme at a rate faster than the competing charge recombination between P_{700}^{+} and F_B^{-}. To link the photochemical and catalytic modules of our half-cell, a short aliphatic or aromatic dithiol molecule forms a coordination bond with an exposed Fe of the F_B cluster of a PSI 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 using a highly active hydrogenase variant from *Clostridium acetobutylicum*, we have achieved a very high rate of light-driven H_2 evolution. This success was due to a combination of several factors: (1) use of a highly active H_2ase variant that had been expressed in *C. acetobutylicum* rather than *E. coli*; (2) the use of phosphate buffer at pH 6.5 instead of Tris-HCl buffer pH 8.3 to increase the concentration of available protons; (3) the use of 1,8-octanedithiol instead of 1,6-hexanedithiol as the molecular wire to avoid steric hindrance; and (4) using cross-linked Cyt c_6 as the electron donor to minimize the diffusion barrier to P_{700}^{+}. Our results show that when ascorbate is the sacrificial donor, 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 µmoles e^{-} PSI^{-1} s^{-1}, assuming a PSI to PSII ratio of 1.8 as occurs in the cyanobacterium *Synechococcus sp.* PCC 7002. The above rate is consistent with the assessment that the catalytic module is not the rate-limiting step in light-driven H_2 evolution. (CaHyd is capable of evolving 6,000 H_2 $protein^{-1}$ s^{-1}, which is equivalent to 12,000 electrons $protein^{-1}$ s^{-1} when electrons are supplied by reduced methyl viologen.) Because PSI is ultimately capable of transferring ~1000 electrons $protein^{-1}$ s^{-1}, we can anticipate another 5-fold improvement may be possible by further adjustment of these variables.

In conclusion, the significantly greater electron throughput by our hybrid biological/organic nanoconstruct over in vivo oxygenic photosynthesis validates the concept of tethering proteins through their physiologically relevant redox cofactors to overcome diffusion-based rate limitations on electron transfer.

Designing Smart, Responsive Communicating Microcapsules from Polymersomes

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The goal of this project will be 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. 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.

The specific objectives of this work will be the following:

(1) Encapsulate and release nanoparticles from polymersomes in response to light and pH.

(2) Use specific adhesion and micro-contact printing to make specific spatial arrays of polymersomes and microparticles.

(3) Demonstrate the collective motion of micron-sized particles in response to light and pH. We will adhere particles on printed arrays. We will combine photoresponsive or pH sensitive polymersomes, equipped with nanoparticles, as signaling particles, and vary the density and spacing of target receiving particles. Upon change in stimulus, we will use video microscopy to observe the collective motion of particles on the surface. Collective motions will be catalogued as a function of interparticle spacing, nanoparticle density, and particle size.

(a) We will perform experiments with multiple signaling particles, with intervening fields of target particles, to understand how competitive fields of stimuli can induce motion of particles in the field.

(b) Additionally, we will compare haptokinesis (in which signaling particles emit nanoparticles that adsorb to substrates) to chemokinesis (in which soluble molecules adsorb to the surface of the surface of the target particles). The latter is potentially more useful, since it is easier to encapsulate and secrete molecules than nanoparticles from signaling vesicles, without any loss of potency.

Thus far, 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 down the adhesion of the substrate, we can make vesicles that migrate over the surface. In the next period, we envision combining these two concepts to test the concepts of particle communication.

Modular Designed Protein Constructions for Solar Generated H_2 From Water

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OVERVIEW OF RESEARCH AIMS

Abundance of solar power has turned attention toward engineering and constructing molecular devices that convert sunlight energy into stored chemical energy useful to mankind. This grant aims to engineer and construct from-scratch novel protein molecules equipped with light-absorbing pigments and redox cofactors organized to promote efficient light-driven splitting of water and catalyze the generation of hydrogen for fuel. The longer-term plans extend to the design of alternative reductive catalytic sites for reduction of carbon dioxide and nitrogen for fuels and valuable chemical resources.

PROGRESS DURING FY 2011

Progress in laboratories across the globe that are aiming to create molecular systems that harvest sunlight for the generation of renewable fuels and green chemical resources have been hindered by the absence of a clear set of generally applicable guidelines for design, engineering and assembly. While biological photosystems continue to play important roles for inspiration and mimicry, they do not illustrate what are the most efficient designs for photochemical energy conversion. This year we have for the first time applied our principles of electron tunneling to create blueprints. These blueprints demonstrate that photochemical efficiencies observed in existing natural photosynthetic reaction center proteins and their synthetic photochemical mimics can be dramatically improved in simple cofactor triads of electron donor, photoactive pigment and electron acceptor with prescribed inter-cofactor distances and selected relative redox potentials.

The blueprints have been applied this year in our own work to the design of a new generation of simple protein constructions (maquettes) developed to carry out a broad range of photochemical catalytic reactions. These synthetic protein maquettes are proving to provide an adaptable scaffold in which to accommodate triads of pigment and redox cofactors. We are working to reproduce in the maquettes the inter-cofactor distances prescribed in triad blueprints. This has involved the redesign of our maquettes, in particular focusing on the development of single chain four and eight a-helix bundles with helical lengths that extend beyond our first generations of synthetic protein maquettes. The longer maquettes are designed to be half as long again as previous maquettes, to accommodate triads separated sufficiently to generate charge separations for times long enough to promote high efficiency millisecond multielectron oxidation-reduction catalysis. These larger proteins have now been demonstrated to be expressible in E. coli.

Designing Colonies of Communicating Microcapsules that Exhibit Collective Behavior

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Funding:	$120,000

Our research is aimed at addressing one of the Grand Challanges for DOE-related research, as articulated in the 2007 Basic Energy Science Advisory Board (BESAC) report: “master energy and information on the nanoscale to create new technologies with capabilities rivaling those of living things.” What is most gratifying in our recent efforts is that we collaborated with two experimental groups to validate our predictions on the behavior of fluid-driven microcapsules on heterogeneous surfaces. We also worked with Dr. Igor Aronson at Argonne National Labs to design biomimetic capsules that undergo autonomous motion in response to mechanical deformation. In addition to the role mechanical deformation, we examined how the mechanical properties of the underlying substrate affect the bonding interactions between a mobile elastic microcapsule and a compliant substrate. Below, we provide a brief summary of these various studies.

We collaborated with researchers at UMass Amherst to experimentally realize our predictions for creating “repair-and go” microcapsules, which deliver nanoparticles to cracks on damaged surfaces and thereby heal the substrate. In this joint effort, we now show experimentally that nanoparticle-containing microcapsules probe a damaged (cracked) surface, and identify its imperfections by depositing the nanoparticles into the cracks. This selective delivery is performed using a polymer surfactant for stabilizing oil droplets in water, where CdSe quantum dots are initially encased in the oil phase. The encased nanoparticles escape into the cracked regions of a SiO_2-coated poly(dimethylsiloxane) substrate as the droplets traverse the surface. This probing, identification, and delivery motif borrows from repair techniques of cellular biology (i.e., the action of leukocytes), replacing complex biological signaling with simple surface energy recognition. This paper will appear in *Nature Nanotechnology*.

We also collaborated with Prof. Alan Russell’s group at the University of Pittsburgh to validate our findings on the behavior of microcapsules on patterned surfaces and realize our predictions for creating “on the fly” cell sorting devices. An emergent method of sorting cells based on differential rolling on chemically patterned substrates holds potential benefits over existing technologies. To validate our previous predictions and to better understand cell rolling on complex surfaces, a microfluidic device with chemically patterned stripes of the cell adhesion molecule P-selectin was designed. The behavior of HL-60 cells rolling under flow was analyzed using a high-resolution visual tracking system. This behavior was then correlated to the findings from our computer simulations. The combination of computational modeling and widely available fabrication techniques described in the resulting paper represents a crucial step toward the successful development of continuous, label-free methods of cell separation based on rolling adhesion.

Theoretical Modeling, Synthesis and Characterization of Self-Healing Coatings

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Funding:	$293,000

Our goal is to design and construct novel materials that undergo structural rearrangement in response to mechanical stress and thereby exhibit self-healing behavior, preventing catastrophic failure of the system. Our self-healing material is composed of nanogels that are crosslinked by both strong, stable bonds and reactive, labile bonds; that is, this material exhibits a “dual-crosslinking.” One of the research challenges was to formulate theoretical and computational models that could capture the behavior of the dual-crosslinked nanogel material and quantify the mechanical performance of the sample. To address this challenge, we developed new approaches for describing the behavior of soft materials that are interconnected by both stable and reactive bonds. Specifically, we made key enhancements to our previous model, resulting in important new theoretical formulations and computational approaches, and significant new findings. First, we exploited the Hierarchical Bell Model (HBM) to simulate cases where the ligands on neighboring nanogels interact through multiple sites and thus, we can more accurately model the experimental systems synthesized by the Matyjaszewski group. The material is roughly 200% stronger than a sample that is crosslinked solely by stable bonds and can still undergo self-repair in response to the tensile deformation. Reports on our findings appeared on a number of web sites, including www.sciencedaily.com, www.physorg.com, www.eurekalert.org, www.futurity.org, and www.nanowerk.com. We also generalized the lattice spring model (LSM) so that the approach would be applicable to a broader range of materials. Specifically, with this new LSM approach, we can model materials with a wider range of Poisson’s ratios than was possible with the standard LSM approach. In addition, we developed an approach for introducing the effects of viscoelasticity.

The main experimental studies were focused on self-healing networks prepared by ATRP using a degenerative self-exchange process. The guidelines from the computational studies were essential for designing and fine-tuning the molecular structures of these self-healing systems. To optimize the performance of this system, we used a relatively soft matrix (poly(butyl acrylate) with Tg = - 50 C) and UV light instead of a radical initiator. This enabled repeated self-mending processes of the bulk material with exposure to UV light, rather than a constant supply of radicals from the initiator (that could be totally consumed). Several cut and self-mending tests were shown to be highly successful. This process received significant attention in various media:

http://www.qmed.com/mpmn/article/41660/self-mending-polymer-could-fix-future-implants
http://sevenhorizons.pbworks.com/w/page/38091623/Self-Healing%20Polymer
http://www.technologyreview.com/biomedicine/27113/?mod=chfeatured&a=f
http://news.softpedia.com/news/Experts-Create-Self-Healing-Polymer-179433.shtml
http://www.rdmag.com/News/2011/01/Materials-Polymer-shows-amazing-self-healing-properties/
http://www.physorg.com/news/2011-01-polymer-amazing-self-healing-properties.html

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

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Funding:	$225,000

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 and sunlight via the hydrogen evolution reaction. The system we focus on is an 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 [FeFe]H cluster and a priori suggests the possibility of stable linkage and easy electron transfer to the cluster.

The hydrogen production cycle of the [FeFe]H cluster and its coupling to a pyrite electrode have been explored in earlier work funded under this program. We found that [FeFe]H does not remain structurally stable in contact with acidified water during the course of the hydrogen evolution reaction. The cluster has to be redesigned in order to be stably attached to the electrode surface and retain its catalytic activity outside the enzyme. This goal has been achieved in more recent work based on ab-initio molecular dynamics simulations. We have designed a catalytic cluster, [FeFe]P, obtained by modification of the [FeFe]H cluster of the di-iron hydrogenase, and functionalized the pyrite (100) surface with it. Remaining stable throughout, the [FeFe]P cluster produces hydrogen from acidified water with a free-energy barrier of less than 8.2 kcal/mol in room temperature simulations. The rate-limiting step in the cycle is the first protonation, subsequent steps are barrier free and fast. A detailed mechanistic analysis of the oxidation-state changes and electron flow during that step has been carried out.

It is known that di-iron hydrogenases are inactivated by oxygen and pyrite decomposes in the presence of oxygen and water. Work in progress on the O_2 sensitivities of [FeFe]P and FeS_2 (100) shows that dissolved oxygen, which is inevitably present in the electrochemical cell, can attack and inactivate the [FeFe]P/FeS_2 system as well. Our next goal is then to design a protective structure which inhibits the attack of the clusters and the exposed FeS_2 sites by dissolved O_2. At question are the optimal composition and internal structure of suitable overlayer molecules as well as the nanoscale structure of the overlayer into which those molecules pack. This overlayer should form densely in the interstices between the clusters but leave open above each cluster nanoscale water channels through which protons can reach the catalytic site.

The last part of our project will be devoted to the challenging task of characterizing the properties of the H_2-evolving catalyst inside the water-filled channels of the protecting overlayer on FeS_2 (100). The main questions that need to be addressed concern the influence of the confining channel, including its length, on the structure and stability of the supported cluster, its sensitivity to O_2, and finally its ability to produce H_2.

Engineering the Interface Between Inorganic Materials and Cells

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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.

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

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Active research to produce energy via biofuel cells, or through the bioconversion of sugars to liquid fuels, offers exciting new alternates to fossil fuel. We focus on the bioconversion of sugars to butanol using a two-enzyme system. While these enzymatic routes offer 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 in an economically viable fashion. We utilize a novel approach to address these limitations. Here, we immobilize enzymes synthesized via recombinant DNA technology. This cell-free enzyme system will be coupled with pervaporation to produce and continuously remove the desired butanol. As a model enzyme with a simple color change for assessing reactivity, we first plan to immobilize beta-galactosidase and determine the optimal substrate geometry (flat, convex, or concave). Preliminary data indicate that crowding and orientation of the immobilized enzymes have a large effect on enzyme kinetics. We will then study separate reactions of immobilized keto-acid decarboxylase and alcohol dehydrogenase to produce butanol ex-vivo.

Biopolymers Containing Unnatural Building Blocks

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The aim of this proposal is to further develop and apply methods to genetically encode unnatural amino acids with novel chemical and physical properties in bacteria. The first effort will focus on the challenging problem of generating metal ion binding sites in proteins. Specifically, we will use structure-based design and molecular evolution methods together with metal ion binding unnatural amino acids to create metalloproteins with novel redox, catalytic and structural properties. In a second effort, we will generate and optimize additional orthogonal tRNA/aminoacyl-tRNA synthetase pairs that will allow us to efficiently introduce multiple, distinct unnatural building blocks into proteins in response to nonsense and frameshift codons. This work should ultimately allow structurally defined abiological biopolymers with new materials properties to be synthesized using the cell's templated biosynthetic machinery.

Using In Vitro Maturation and Cell-Free Evolution to Understand (FeFe)hydrogenase Activation and Active Site Constraints

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The first project objective is to elucidate the substrates and mechanisms for assembly and maturation of the 6Fe-6S active site of [FeFe] hydrogenases. An early in vitro maturation method was developed using an E.coli cell extract in which the three required maturases had been expressed and activated. The extract was also dialyzed to remove small molecules. We showed, for the first time, that activation of the purified apoenzyme was significantly enhanced by incubating this extract in the presence of S-adenosyl methionine, Fe(II), sulfide, and 20 amino acids. A design of experiment investigation then showed that tyrosine was required and cysteine was beneficial for maturation. Further investigation showed that the para-hydroxyl substituent of tyrosine was required for efficient activation. An improved maturation procedure was then developed, in which the three maturase proteins were expressed separately to avoid in vivo maturase interactions. Such interactions were thought to be important for function, and we sought to gain control over this portion of the maturation mechanism. In contrast to previous inferences, efficient apoenzyme activation was observed using the separately produced maturases. This new system enabled the production of much larger quantities of in vitro activated [FeFe] hydrogenase. This, in turn, enabled high resolution Fourier transform infrared spectros-copy (FTIR) analysis of the C-O and C-N stretches associated with the cyanide and carbon monoxide adducts in the 6Fe-6S active site. Isotopic labeling of tyrosine then conclusively showed that all three of the CO and both of the CN moieties in the active site are derived from tyrosine. Further evaluation has shown, for the first time, catalytic function (i.e., multiple turnovers) for each of the maturases when functioning in the in vitro maturation system.

The second project objective is to gain better understanding of the impact of the polypeptide scaffolding on hydrogenase activity. The expression gene for the CpI [FeFe] hydrogenase from Clostridium pasteurianum was extensively mutated using nucleotide analogs, and isolates were identified that retained at least partial activity and also displayed increased stability during oxygen exposure. The most interesting isolate contained 13 mutations and was extensively analyzed. When two of the amino acid changes were reversed, full activity was restored. Three different mutations increased oxygen tolerance. Unexpectedly, none of these mutations are near the active site 6Fe-6S H-cluster, but four of the five mutations are close to the proximal 4Fe-4S center that either donates electrons to the active site H-cluster or receives them, depending on the direction of catalysis. These results suggest that the function of this ancillary iron-sulfur center has a stronger than expected influence on enzyme function. During this work, we also observed that oxygen inactivation of [FeFe] hydrogenases can be substantially reversed in contrast to general belief. The reversibility also appears to be influenced by the ancillary Fe-S center. A mutational library is now being constructed to assess the function of the amino acids surrounding this ancillary center as well as those that support the active site.

During the course of these investigations, a number of methods were developed of general utility to this field of research. These include (1) the in vitro hydrogenase maturation protocols, (2) a procedure for producing high levels of maturases and hydrogenases in E.coli cultures, (3) improved methods for producing and screening hydrogenase mutants, and (4) a new method for assessing sustained hydrogen production activity while using a reduced ferredoxin protein as the electron donor. In particular, the last method is very important as it will now allow us to screen for mutants with increased oxygen stability while they are actively making hydrogen. In addition, this method suggests the feasibility for cost-effectively producing hydrogen from biomass hydrolysates. A new research program has now been initiated to develop technology for the large scale production of hydrogen from biomass hydrolysates.

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

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Funding:	$250,000

It is now broadly appreciated that microparticles dispersed in low molecular weight liquid crystals (LMWLCs) generate topological defects within the LC phase. The topological defects can be point, Saturn ring and boojum, depending upon factors such as the particle size and surface chemistry. It is also understood that the topological defects formed in the LC can mediate inter-particle interactions that lead to the formation of particle arrays and formation of chains. Whereas past studies have focused on LMWLCs, recent studies at UW-Madison have provided the first experimental characterization of an investigation of the orientational ordering in liquid crystalline elastomers (LCEs) around microparticles. A key accomplishment of the UW-Madison research has been the development of experimental procedures that allow the incorporation of microparticles in LCEs. Using such procedures, we have been able to demonstrate the presence of “soft elasticity” in these particle-containing LCEs.

The interpretation of the experimental results outlined above requires that new models be developed for liquid crystalline elastomers. There are no such models available in the literature. Our first step has been to develop a coarse grained representation of the elastomer in which the crosslinker molecules have been represented by either flexible or rigid oligomeric units. In the latter case, crosslinker molecules enhance the anisotropic nature of the LCE sample and provide stability to the material. In the rigid case, the crosslinkers and the mesogens (LC) molecules are represented by ellipsoidal particles.

At equilibrium, in the absence of an applied stress, our model LCEs exhibit several nematic domains whose directors are independent of each other. These results confirm that the proposed model is capable of describing a polydomain state, as observed in our experimental studies. As a uniaxial stress is applied, the system initially remains in a polydomain state, but these 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 curve for the model LCE is consistent with those observed in our experiments. We have also observed that the domains rotate with the application of stress, but they grow in size only marginally. This leads us to conclude that the polydomain-to-monodomain transition occurs through a rotation of nematic domains, as opposed to a growth of such domains. Consistent with experimental observations, we also find 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.

Considerable progress has also been made in our ability to synthesize and model colloidal liquid crystal gels consisting of colloidal particles. We have shown that by controlling the size of particles and their chemistry, one can alter interactions between them over a range of energies that encompasses several decades of magnitude in kT.

Optical and Electro-Optic Modulation of Biomimetically-Functionalized Nanotubes

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PROGRAM SCOPE

The goals of the program are to develop a fundamental understanding of the light-induced changes on the electronic properties of functionalized carbon nanotubes through a combination of new functionalization chemistry, probing the electrical and optical response of the nanotube/chromophore hybrids, and interpretation of the results with theory/modeling. Nanotube-based electronic and electro-optic devices have long been cited as potentially revolutionary. Despite much initial progress, the promised applications have been slow in coming, due first and foremost to the large diversity in size and chirality of single-wall nanotubes and due to limitations in the strength of interaction with light. In our work, we focus specifically on the development and understanding of functionalization for the optimization of electro-optic properties. And we do so in the context of, and using methods compatible with, the recent important advances in nanotube purification, and leveraging the long-standing understanding and accomplishments in the creation of high-mobility nanotube devices. The project utilizes a unique set of expertise covering materials chemistry, physics, and theory.

RECENT PROGRESS

To probe the chromophore/SWNT interface, we started with spectroscopic analysis the hybrid systems using complementary experimental techniques and ab initio calculations. For the chromophore, we use Disperse Red 1 (DR1), a well-studied and commercially available azobenzene chromophore, with a series of three increasing tether strengths: (1) unmodified DR1 with no added tether (DR1U), (2) anthracene-functionalized DR1 (DR1A), and (3) pyrene-functionalized DR1 (DR1P) (see Scheme 1). The first part of our studies on thin-films shows that the binding energy and hence the surface coverage of the chromophores on the nanotubes is strongly influenced by the strength of the tether; we also address the question of the orientation of the molecules on the nanotubes by optical second harmonic generation (SHG) measurements. The second part of our studies focuses on the solution characterization of the hybrids to evaluate the nature of the electronic coupling.

DOE National Laboratories

Bioinspired Materials

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The synthesis and characterization of novel bioinspired hybrid materials can mimic living systems in their abilities to respond to the environment and self-assemble hierarchically. To facilitate a bottom-up approach to nanocomposite materials design, these materials use (1) organic templates coupled with mineralization proteins to direct the biomineralization processes and (2) aptamers for achieving specificity of non-covalent binding. Understanding guiding mechanisms of assembly across multiple length scales through combination of experiment and theory involves advanced solid-state NMR techniques for investigating interactions of the organic templates with inorganic components.

SPECIFIC THRUSTS

Development of multiscale self-assembling bioinspired hybrid materials using bottom-up approaches: We are designing hierarchically self-assembling templates (synthetic polymers as well as protein and peptide based templates), and using bioinspired methods for room temperature synthesis of several energy-relevant hybrid materials with hierarchical order difficult to synthesize otherwise.

Development of techniques to probe assembly at multiple length scales and properties of these nanocomposites: We are using a combination of solid-state nuclear magnetic resonance (NMR), scattering, and electron microscopy techniques to investigate the nanostructure and composition, and other characterization techniques to investigate the magneto-mechanical properties of these hybrid materials. This will result in fundamental insights into the design principles for synthesizing and organizing nanocrystals using bioinspired approaches.

Development of computational methods for understanding general design rules for self-assembled polymer nanocomposites: We are developing and implementing molecular simulations using high performance computational approaches as a powerful tool to understand the underlying principles of self-assembly of complex structures, phase transformation between competing phases, as well as the response of a self assembled system to external stimuli.

Early Career: Real-Time Studies of Nucleation, Growth and Development of Ferromagnetism in Individual Protein-Templated Magnetic….

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Magnetic nanoparticles with narrow size distribution, large magnetic moment, and controlled magnetic anisotropy have important technological applications in a wide variety of areas, ranging from data storage and quantum computing, to magnetocaloric refrigeration and cancer therapy. Bio-inspired synthetic routes offer room-temperature pathways to the production of a variety of magnetic nanostructures with exceptional control over nanoparticle formation using biomolecules as matrices, scaffolds and templating agents; thus permitting the fabrication of magnetic nanocrystals with shapes and sizes not realizable via conventional inorganic chemical techniques. However, despite significant research effort in this area, fundamental understanding of the microscopic mechanisms is lacking on how the supramolecular assembly of biomolecules dictates shape, size and structure of the resulting crystals and how the nucleation and growth processes in biomimetic systems affect functional properties of resulting nanoparticles.

Utilizing advanced electron microscopy techniques, the proposed research offers an unprecedented opportunity for determining the nature of macromolecule-mediated nanoparticle formation: i.e., the mechanism of particle nucleation, growth, the emergence of crystal structure, and the development of ferromagnetism in the individual bio-templated magnetic nanocrystal. Expected experimental findings will be broadly applied to the synthesis of various biomimetic magnetic nanomaterials with controlled and well-defined properties. The proposed work addresses one of the five “Grand Challenges” identified by the DOE BES Advisory Council, specifically: How do remarkable properties of matter emerge from the complex correlations of atomic or electronic constituents and how can we control these properties? The proposed work will lead to the further advancement of the bioinspired methods, and will facilitate rational engineering of various biomimetic magnetic nanomaterials with the properties relevant to DOE's mission.

Dynamics of Granular Materials

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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 3 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 correlations in active transport of cargo along cytoskeletal networks. For all these model systems we have developed theoretical description leading to the prediction and control of emergent self-assembled structures.

In the next 3 years we will explore new approaches to the synthesis and discovery of a broad range of self-assembled bioinspired materials stemming from the advance of our program. Examples include functional 2D and 3D dynamic colloidal structures built from elementary functionalized sub-units that are transported into place and then assembled by self-propelled autonomous agents, such as swimming bacteria or synthetic swimmers, that are controlled by electric or magnetic fields.

Nanostructured Biocomposite Materials for Energy Transduction

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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.

Bio-Inspired Programmable Assembly

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The main focus of this effort is the development of novel bio-inspired approaches for the creation of well defined nanoscale architectures, from clusters to 3D structures, that incorporate inorganic nano-objects and biological molecules into a hybrid system. Our methodology toward this goal utilizes a strategy of bio-programmable assembly, in which the high degree of selectivity and addressability of biomolecules such as nucleic acids, peptides and proteins is used to guide interactions of encoded nano-objects, thus, leading to structure formation.

PROGRESS

The first demonstration of designed self-assembled multicomponent system with tunable lattices. We showed the first successful assembly of 3D multicomponent nanoscale superlattices with incorporated particles and fluorescent ghost molecules and showed that assembled structures can be dynamically tuned. The combination of synchrotron based structural methods and time-resolved optical imaging techniques allowed for determination of the relationship between the structure and fluorescent properties of 3D arrays. Our study tackles important questions about the self-assembly of systems from components of multiple types.

Assemblies containing particles of different types and sizes. We initiated studies of systems containing particles of different sizes and different DNA shells to probe how a balance between geometrical factors, entropy and interactions affects a phase formation. This allows addressing a question about influence of particle “softness” on a phase diagram of binary mixtures. We also started a study on the assembly of binary systems comprised of particles with different inorganic cores, including gold particles with sizes ranges between 5 to 50 nm with thiol-bounded DNA, and particles of silver, iron oxide, or cadmium selenide functionalized with complementary DNA strands. We developed a general strategy for DNA functionalization of different type particles. Our preliminary results indicate that these particles can bind tens of DNA strands using the developed functionalization method. SAXS and electron microscopy were applied for the preliminary characterization of a phase behavior of assembled systems.

Anisotropic nano-objects: interactions and assembly behavior. We have started investigating a relationship between geometrical factors of nano-objects and molecular effects, such as chain entropy, chain-chain interactions and directional binding, on the formation of 3D phases. We have developed methods of fabrication of nanoscale objects with rod- and cube- like shapes in the size regime from 10 nm to 65 nm for palladium, gold, gold/silver (core/shell) particles. Our experiments reveal a remarkably unique behavior for rods interacting via DNA: 1D structures can emerge via spontaneous symmetry breaking of underlying interactions. We observed a self-assembly of rods in a quasi-1D ladder-like ribbons with a side-by-side arrangement, as well as in structures with alternating rods and spheres. We also studied the phase behavior of cubes connected with DNA linker and organic linkers. The observed diversity of 3d structures, including simple cubic, fcc, and bcc with different relative cube orientation. The phase transformation in cubes assemblies induced by cube to sphere shape-shifts was experimentally observed for the first time and in accord with theoretical predictions.

Soft Matter and Biomaterials

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Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$930,000

The primary goal of the program 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. We use synchrotron x-ray scattering, scanning probe and optical microscopy techniques to study fundamental properties of complex fluids, simple liquids, macromolecular assemblies, liquid crystals, polymers, and biomolecular materials. Key progress in FY 2011 include the following:

(1) Grazing incident angle scattering studies of TMVY virus monolayers on a mixed lipid surface revealed two new forms of 2D crystals of TYMV, one consisting of a square array with a double-square rectangular unit cell and the other a centered-rectangular crystal. Comparison with the particle's shape and surface patchiness, deduced from the known atomic coordinates of the virus, indicate that these structures are stabilized by both hydrophobic patch-patch attractions and interparticle contacts that exhibit electrostatic and shape complementarity.

(2) X-ray reflectivity measurements have been carried out to determine the structure at the solid/liquid (s/l) interface between a bulk alcohol (octadecanol: C18OH) and sapphire, (0001), a solid support. Over a range of temperature (about 30 °C) above the freezing point of the alcohol an extremely well defined monolayer is stable at the solid interface, with surface-normal, rather than surface-parallel, molecules. This reversible formation of an interfacial monolayer is reminiscent of surface freezing at the solid/vapor

(s/v) interface where the much larger temperature range for the solid interface is consistent with the much stronger surface interaction.

(3) The liquid/liquid interface between aqueous solutions containing mM quantities of Cetyl trimethylammonium bromide (CTAB), a cationic surfactants, and n-alkanes has been investigated. At high temperatures, the surfactants form a thin liquid-like monolayer at the bulk alkane/water interface. Upon cooling, this layer undergoes a freezing transition well above the bulk freezing temperature of the alkanes, surfactant and water, forming a solid monolayer of densely-packed, extended, surface-normal-aligned molecules where the alkane and CTAB chains are interdigitated. This surface frozen state represents the first example of surface freezing at a liquid/liquid interface.

(4) The trapping of air at the interface between water and a hydrophobic silicon surface decorated with hexagonal arrays of ~20 nm-sized parabolic cavities prepared using diblock-copolymer lithography has been investigated. We have found that air nanobubbles form inside the cavities where the bubble's shape depends on the geometry and hydrophobicity of the cavity wall. These results improve our understanding of nanobubble formation and may guide the design of novel superhydrophobic nanostructured surfaces.

Biomolecular Materials Program

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Students:	4 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding:	$850,000

Our underlying premise is that organisms evolved molecules, structures, processes, and approaches to achieve functions that can be used or mimicked to form materials, devices, and concepts for application in nonliving environments. This differs from Biomaterials work which seeks to develop solutions-implants, artificial organs, drug delivery systems--to biomedical problems afflicting humans. The program focuses on (1) the design and synthesis of proteins, dendrimers, DNA oligomers and biological structures such as viral capsids for spatial patterning of organic and inorganic functional assemblies and (2) studies of living/nonliving interfaces to develop materials with biological or similar materials serving as coatings for non-living materials (and the converse), as well as for the development of hybrid materials and devices that exploit the specific advantages of both living and nonliving materials. The focus here is on lipid, carbohydrate and protein structures, including lipid bilayer membranes. Theory work supports the experimental research in these areas. The program has completed another successful year, with 12 publications, including one in *Science*, three in *Nano Letters*, four in *JACS*. The project is being terminated at the end of 2012, and the focus will then be on completing work that has begun and writing up the results for publication.

Directed Organization of Functional Materials at Inorganic-Macromolecular Interfaces

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Students:	0 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding:	$900,000

The purpose of this project is to develop a quantitative physical picture of macromolecular organization and its relationship to function and to use macromolecular organization to derive new functionality. The research is divided into three subtasks: (1) the fabrication of bio-nanoelectronic devices based on lipid-protein layers assembled on "1D" nanowires, (2) the creation of artificial light harvesting complexes using virus-DNA origami arrays on 2D chemical templates, and (3) the determination of 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
- Use organization to derive new functionality and explore the correlation between these two phenomena

The proposed research directly addresses one of the five Grand Challanges identified in the BES report, "Directing Matter and Energy: Five Challenges for Science and the Imagination" in that it seeks to "…master energy and information on the nanoscale to create new technologies with capabilities rivaling those of living things."

Cooperative Phenomena

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Funding: $80,000

The goal of this project, which is part of a larger project at Sandia National Laboratories, 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. To this end, our studies have previously been aimed at understanding the mechanisms of templated composite material formation, the development of methods to create patterned thin films with nanoporous architectures, and the creation of new material functionalities by incorporating active molecular and/or biomolecular components into patterned and templated oxide materials.

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 control the properties of encapsulated nanomaterials. 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.

Molecularly Engineered Biomimetric Nanoassemblies

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Sinha, Sunil K., CALIFORNIA, UNIVERSITY OF SAN DIEGO
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Funding: $730,000

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: (1) photo-induced charge separation and (2) 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.

Active Assembly of Dynamic and Adaptable Materials

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Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding:	$1,290,000

The objective of this project is to exploit key strategies 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 consuming “nano-robots” that can duplicate many of the complex emergent behaviors of living systems within artificial nanocomposites. Program components include Active Protein Assemblies, in which we are deploying cellular proteins in artificial environments. Key proteins include tubulin, which can be programmed to reversibly polymerize hollow cytoskeletal fibers called microtubules, and the motor protein kinesin, which transports “nanocargo” by “walking” along microtubule networks. Program components also include Artificial Microtubules, in which we are developing artificial monomers that incorporate key design features of tubulin to create simple and robust programmable nanofibers.

Highlights in the Active Protein Assemblies task include the following:

- Motor Proteins – We are now exploring dynein motors that walk along microtubules in the opposite polar direction than kinesin motors to facilitate “two-way” traffic in transportation systems.
- Microtubules – Microtubules are known to grow by adding or subtracting tubulin dimers from the ends of the growing tube. We now have experimental evidence that very long microtubules can be produced via the fusion and annealing of existing microtubule segments, which represents a new mechanism for microtubule formation.

Highlights on the Artificial Microtubule task include the following:

- Dendrimers – We have produced dendrimeric “monomers” that can be thermally programmed to polymerize and depolymerize much like natural microtubules based on reversible Diels-Alder reactions.

- Theory/Modeling – We have developed molecular dynamics simulations to understand the basics of microtubule assembly. Simulations show that microtubules only form for monomers that have the proper shape, as well as the strength, distribution, and local symmetry of binding sites.
- Peptides – We are experimentally testing the design rules derived from the Modeling task using branched polypeptide "monomers." By varying peptide sequences, we have systematically varied the locations of acid-base, hydrogen bonding, and hydrophobic/hydrophilic sites. Assembly experiments with the monomers have identified specific distributions that lead to fiber formation.

Proposed future work includes the following:

- Active Protein Assemblies – We plan to investigate two demonstrations illustrating the use of active proteins. We have created an "on-chip" switch-yard and transportation system in which electric fields and motor proteins will be used to route cargo through a maze of interconnected microchannels. We will integrate our polar artificial microtubule organizing centers with microtubules, kinesin, and dynein to create programmable arrays of quantum dot "dyes" in analogy to the color changing system of the chameleon.
- Artificial Microtubules – (a) Dendrimers – Currently, our dendrimers only function in organic solvents, so we plan to functionalize the dendrites so that their solubility and programmability can be extended into aqueous environments. (b) Peptides – While current constructs form nanofibers, their behavior is not programmable. Here we plan to incorporate switchable molecules that have been developed in a sister BES-funded program (Molecular Nanocomposites) into the polypeptides to program polymerization using heat, light, or electric fields.

Molecular Nanocomposites

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Funding:	$1,495,000

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 & 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.

Recent highlights of the Adaptive and Reconfigurable Nanocomposites sub-task include the following:

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

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

(3) Magnetic Nanoparticles – New methods have been developed to synthesize monodisperse magnetite nanoparticles for magnetically programmable nanocomposites.

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

Progress in the Complex Nanocomposites sub-task has advanced the field of molecular nanocomposites in four substantive directions:

(1) Electrostatically Mediated Self-assembly – The first single crystal X-ray structural determination has been made for nanosheets formed by assembly of oppositely charged porphyrin building blocks (cooperative binary ionic, CBI, solids). Hydrogen generation has been demonstrated using hierarchical hybrids consisting of catalytic nanoparticles grown on light-harvesting CBI substructures.

(2) Cooperative Self-assembly (CSA) – Well-defined porphyrin nanostructures within amphiphilic block co-polymer micelles were prepared through the CSA of active and amphiphilic molecular building blocks. The self-assembly process was used direct or confine nucleation and growth, allowing fine-tuning of 1-3D active nanomaterials with controlled external morphology and hierarchical function.

(3) Pressure-directed assembly (PDA) – We showed for the first time that application and release of a hydrostatic and/or uniaxial pressure field causes the unit cell of a 3D nanoparticle 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.

(4) Protocellular Architectures - Architectures composed of fluid, dynamically reconfigurable phospholipid bilayers supported on self-assembled nanoporous silica particles have been developed as platforms in which to recapitulate the compartmentalized chemistry and function of living cells. By incorporation of enzymes and molecular machinery within the ‘protocells’ and selective ion channels and light harvesting complexes within the supported lipid bilayers, we expect to develop new classes of protocells that perform rudimentary, self-sustaining life-like functions.

Future work in the Adaptive and Reconfigurable Nanocomposites sub-task will include the following:

(1) Programmable Molecules – Surfactants are being prepared that can be switched by light and electrochemical voltages, with tails that are adapted for insertion into lipids and polymersomes.

(2) Programmable Assemblies – Work will focus on understanding the mechanisms by which programmable molecules induce the reversible formation of domains and 3D structures such as nanotubes.

(3) Magnetic Nanoparticles – Switchable molecules will be introduced into nanoparticle surfaces to explore what nanocomposite architectures can be achieved by coupling magnetic alignment with programmable interparticle interactions.

In addition to continuing to extend our understanding of self-assembly, the Complex Nanocomposites sub-task is adding a significant new direction through the addition of former SNL Truman Fellow, Bryan Kaehr, to our team. Bryan, working with the Brinker group has developed Cell-Directed Assembly as a general route to synthesize cell/silica composites (CSCs), wherein mammalian cells serve as templates to direct their replication in silico. Inter- and intracellular structural heterogeneity and nano- to macro-scale feature size is captured and preserved in CSCs following drying calcination and conversion to conductive carbon replicas. The structural and behavioral malleability of the starting material (cultured cells) provides enormous opportunities to develop robust and economical biocomposite materials with programmed structures and functions.

Molecularly Engineered Biomimetic Nanoassemblies

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Students:	Postdoctoral Fellow(s), Graduate(s), 1 Undergraduate(s)
Funding:	$70,000

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.

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.

Protein Biotemplates for Self-Assembly of Nanostructures from Clathrin Materials	
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Students:	2 Postdoctoral Fellow(s), 7 Graduate(s), 0 Undergraduate(s)
Funding:	$681,000

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.

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

The goal of this project is to determine the active atomic-level structure of photocatalytic nanomaterials under near reaction conditions especially as it relates to solar fuel generation. The PI proposes to modify an in situ environmental transmission electron microscope to allow light irradiation of photocatalysts in the presence of reactive gases. Specifically the PI will:

- Develop in situ instrumentation to permit atomic level observation of catalytically active nanomaterials in the presence of reactive gases and heat *under photon irradiation of variable wavelength and intensity.*
- Determine the phase transformations that take place in titania-based nanomaterials during in situ photon irradiation at different wavelengths and intensities under gas conditions relevant to photocatalytic conversion.
- Use monochromated electron energy-loss spectroscopy to investigate the changes in electronic structure of titania-based photocatalysts during in situ photon irradiation at different wavelengths and intensities.

This proposal addresses a research topic of significant interest to DOE. The proposed project provides a new approach for characterizing active photocatalysts for solar fuel production.

Nanoscale Imaging of Electrostatic and Magnetic Fields

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Funding:	$140,000

Nanoscale electromagnetic fields are essential for the function and operation of many nanostructured objects and devices. Important examples include elemental and compound semiconductor p-n junctions and non-volatile magnetic storage media. Theory and modeling can be used to estimate field strengths but direct measurements are preferable for smaller dimensions, especially to understand and control the effects of local inhomogeneities and two-dimensional dopant diffusion on macroscopic properties. Our research program focuses on the observation and qualification of electrostatic potential distributions in and around complex heterojunctions, and the micromagnetic structure of ferromagnetic thin films and small particles. The primary characterization method is the technique of off-axis electron holography, which provides access to the change in phase of the electron wave after it has passed through the specimen region of interest. These phase changes can be directly related to the electromagnetic fields of the object. Coupled with recent developments in digital recording and data processing, electron holography can be used to extract quantitative details about electromagnetic fields at the nanoscale, which can then lead to a better theoretical understanding of their effects.

Quantitative Electron Nanodiffraction

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Funding:	$150,000

Artificial oxide heterostructures show great promise as a new generation of electronic materials, in which novel electronic properties, such as high mobility, magnetism, and quantum 2D devices may be engineered in a controlled manner using layer-by-layer growth. Over the past year, we have succeeded in obtaining electron energy loss spectra from individual atomic columns across the interfaces in a LaSrMnO Ruddleson-Popper manganite digital superlattice, together with atomic-resolution HAADF STEM images. The material was grown by our collaborators in the Bhattacharya group at ANL. This EELS data, in the near-edge fine structure, shows local changes in coordination, valence and chemistry at the interface, possibly due to tilting of oxygen octahedra. A pre-edge feature, which occurs only between double layers of La-O, is mapped out in real-space at atomic resolution for the first time. The Mn valence is found to be modulated within the superlattice. Electron diffraction patterns were also analyzed as a function of temperature, where superlattice reflections show the perfection of the superlattice, and a structural phase transition at around 100 K correlates with bulk magnetization measurements. We are particularly interested in the possibility of a 2D magnetic transition at the interface (indicated in bulk magnetization measurements), which would cause localized astigmatism in atomic-resolution phase-contrast images. An analysis of this effect, and of the effect of changes in the layer-by-layer stacking sequence on forbidden reflections in oxide superlattices has also been presented. Work continues to understand the detailed atomic nature of this low-temperature interfacial phase transition using the very powerful combination of electron diffraction, imaging and energy-loss spectroscopy.

In addition, we have embarked on a study of the occupancy sites of Cu dopants in the new topological insulator material Bi_2Te_3.

This work is in collaboration with the Z.X. Shen group at Stanford Applied Physics. Samples have been obtained and prepared for TEM, which, for these layer structures, is extremely difficult. They show remarkable persistent spin currents on all faces, which do not require atomic cleanliness, and which may be useful as Qbits for quantum computing.

Structural Studies of Amorphous Materials by Fluctuation Electron Microscopy

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Funding:	$215,000

Fluctuation electron microscopy (FEM) is a relatively new transmission electron microscopy technique for studying medium-range order (MRO) in amorphous materials. Medium-range order, at length scales from 0.5 – 2.0 nm, is hard to quantify by diffraction alone, or by direct imaging in the TEM, because of the averaging that is inherent in the signals. The pair distribution function (PDF) obtained by diffraction is sensitive to short-range order, out to ~1.0 nm. High-resolution imaging in amorphous materials is inherently limited by the projection through the sample thickness, which is usually greater than 10 nm in self-supporting films. FEM gains its sensitivity to MRO by using a hybrid of both diffraction and imaging. Essentially, FEM examines the spatial variations (fluctuations) in diffracted intensity between small volumes in the sample (essentially 0.5 – 2.0-nm-wide columns). The statistical variance of the scattering is strongly dependent on the higher order, 4-body, pair-pair distribution function of atoms in the sample. Diffraction alone is dependent on 2-body correlations, which become averaged away beyond about 1 nm in amorphous materials. (In crystals the PDF range can extend much further.) It is this sensitivity to higher-order correlations that gives the FEM variance the ability to detect the subtle presence of medium-range order in the sample, despite all the averaging. However, so far it has not been possible to invert FEM data to obtain the 4-body function directly. This lack of quantitative methodology makes FEM data interpretation a matter of hit-or-miss model building and FEM simulation. With skill and patience, this can be done. However, for FEM to become a mainstream tool, this needs to be remedied.

The objectives of this proposal are to make FEM a more quantitative method and to apply it to a number of technologically interesting amorphous materials.

The primary goals of the proposal are two-fold:

(1) Develop the quantitative aspects of the FEM technique. This will involve exploring new experimental methods using the new aberration-corrected electron microscopes at ASU, as well as developing advanced experimentally constrained molecular relaxation computational methods (ECMR) for data analysis.

(2) Apply the FEM method to interesting and technologically important families of amorphous materials. These include amorphous zircons ($ZrSiO_4$) and related framework oxides for potential nuclear waste storage, and negative thermal expansion tungsten bronzes (ZrW_2O_8). This will yield new knowledge about the structures of these important complex oxide materials, and will help to focus the efforts of goal 1 onto real-world problems.

An important outcome of this project will be a new quantitative analytical tool for exploring medium-range ordering in amorphous materials, which will provide a much-needed complement to the PDF technique obtained by diffraction for short-range ordering.

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

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Funding:	$160,000

The aim of this research program is to develop a robust method to quantify the atomic scale changes in structure, composition and bonding that occur at grain boundaries. Although scanning transmission electron microscopy has long had the ability to deliver atomic resolution Z-contrast images, interpretation of the image contrast and subsequently the properties of the material being studied, has primarily been on an image by image basis – in some cases extrapolating a single image to represent the properties of all grain boundaries in a materials system. However, 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, 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. This research program will significantly extend the previous analysis by applying the methods to grain boundaries, i.e., extended defects where the symmetry changes. Experiments will be performed on state-of-the-art aberration corrected microscopes at UC-Davis and Lawrence Livermore National Laboratory and 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 specifically on [001] tilt grain boundaries in $SrTiO_3$ to act as a prototype system for perovskite materials being developed as superconductors, ferroelectrics, and ionic conductors. These grain boundaries will be fabricated through a collaboration with the University of Tokyo and feature both pristine and doped grain boundary cores. 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.

New In Situ Analytical Electron Microscopy for Understanding Structure Evolution and Composition

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Funding:	$158,000

Materials for electrochemical energy storage, in particular those used in a rechargeable way, are inherently complex. Novel oxides and multifunctional nanostructures of oxides are at the heart of electrochemical energy storage technologies. Advances in understanding and controlling the dynamic behaviors in these complex oxides, particularly at the interfaces, during electrochemical processes will catalyze creative design concepts for new materials with enhanced and better-understood properties. We have developed the novel in-situ analytical transmission electron microscopy (ATEM) for understanding the chemistry and structure evolution of the electrode/electrolyte bulk and interfaces during electrochemical process of all solid state batteries. Several major challenges have been tackled to realize our proposed idea. We have used pulsed laser deposition technique to fabricate multi-layer oxides batteries. We have set up an in situ TEM apparatus that enables vacuum transfer (controlled atmosphere), temperature control and electric bias. The model system of spinel materials, whose delithiation process during the charging of the lithium ion battery proceeds as a two-phase reaction, will be studied. We will be able to obtain the time resolution and special resolution that are highly relevant to the lithium ion batteries, to answer the scientific questions, such as how the two-phase boundary move in the oxide when lithium is being removed, which have not been possible to explore with conventional TEM. New materials systems that have complex composite structures will be explored using the newly developed tool. The capability developed in the proposed work will have broad and significant impact on the in-situ characterization of electrochemical active materials in batteries, fuel cells, supercapacitors etc.

Phonons and Electrons in Thin Complex Oxides

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The objective of this program is to develop new approaches to understand and control phase transformations in complex oxide thin films as their dimensions approach the nanoscale. The project focuses on epitaxial oxides with the perovskite structure, exhibiting ferroelectric and metal-insulator transitions, respectively. A major goal is to provide a fundamental understanding of how these transitions are controlled by film strain, the atomic structure of interfaces and dimensionality. Perovskite titanates will be developed with high structural perfection, high purity and low intrinsic defect concentrations by new oxide molecular beam epitaxy approaches. The project builds on the unique capabilities of scanning transmission electron microscopy techniques, in particular, quantitative high-angle annular dark-field imaging and diffraction techniques, which will be further developed in this program. The combination of macroscopic and microscopic techniques will provide a wealth of information about transport, vibrational modes and defects in ultrathin films.

Hydrogen Generation Using Integrated Photovoltaic and Photoelectrochemical Cells

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Funding:	$150,000

In the past year, we have continued our efforts on developing novel nanostructures of metal oxides (MOs) for solar hydrogen generation based on photoelectrochemical (PEC). Materials investigated are focused on 1D MO nanostructures of TiO_2, WO_3, ZnO, and Fe_2O_3 in conjunction with quantum dot (QD) sensitization and doping to alter their electronic band structures for both visible light absorption and for facilitating interfacial charge transport. Specifically, we have synthesized various nanostructures of α-Fe_2O_3 nanostructures and characterized their PEC and charge carrier dynamics. Even though the charge carrier lifetime is generally very short (major decay in < 1 ps), strong photocurrent has been observed and correlated to the small amplitude, slow delay component of the charge carriers.

Another major discovery is that hydrogen treatment of MOs can effectively alter their bandgap structures to improve PEC performance, including TiO_2, ZnO, and WO_3. This is attributed to increased electron donor density due to increased density of oxygen vacancies as a result of hydrogen treatment. Preliminary dynamics studies have been carried out to directly probe the bandgap states for the first time and the results are in preparation for publication. In addition, we explored the possibility of using metal nanoparticles as sensitizers for MOs and found that under the conditions studied, no sensitization is possible, in contrast to studies reported by others previously. The reason for the different observations is currently under investigation. Overall, we have made substantial progress in our research on PEC hydrogen generation using nanocomposite structures, and further work is underway to understand deeper the fundamental mechanisms underlying the interfacial charge transfer and transport processes using ultrafast laser and other experimental techniques.

Experimental Vector Field Electron Tomography of Magnetic Objects

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Funding: $175,000

During FY 2011, we carried out research on the following topics: 2D frustrated magnetic systems, and 3D magnetization state determination. In collaboration with the group of Dr. Amanda Petford-Long at the Argonne National Laboratory, we worked out analytical expressions for the magnetostatic interaction energy between thin islands of rectangular and stadium shape, and applied these energy expressions to the modeling of the behavior of arrays of closely spaced island in a spin-ice lattice. We have modeled (via a Monte Carlo approach) the behavior of a square spin-ice lattice as a function of the applied magnetic field. Our observations of magnetic monopole-type behavior were published in PRB (83:174431, 2011), and comparisons of MFM measurements with MC simulations are currently under review (submitted to PRB).

In the area of vector field electron tomography (VFET), we have made progress in the implementation of an iterative approach to the 3D reconstruction of the magnetic vector potential. Our earlier work successfully reconstructed the vector potential based on filtered back-projection, but we believe that iterative procedures will be able to improve both the spatial resolution and the accuracy of the reconstructions. We have also commenced the analysis of the use of prior knowledge in VFET. We know, a priori, that the magnetization can only be non-zero inside the sample; this knowledge provides a constraint that we intend to incorporate in to the reconstruction algorithm. Furthermore, we are exploring an approach to the Transport-of-Intensity Equation formalism that will allow us to directly determine only the magnetic component of the electron phase shift, without the need to separate it from the electrostatic component. (The Fourier spectra of these two components are quite different, so having the ability to determine one without needing the other will presumably improve the spatial resolution as well.)

Finally, we have started work, once again with our colleagues at ANL, on the analysis of “resolution” in Lorentz microscopy. This is a poorly defined concept, since it appears to be tied to the sample as well as the microscope, so we are taking a close look at the theory of Lorentz image formation in the context of aberration correction. The goal is to create a clear definition of magnetic resolution in Lorentz microscopy.

Grain Boundary Complexions and Transitions in Doped Silicon

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Funding: $95,000

This project systematically investigates the formation and stability of grain boundary phases (also called "complexions") and the associated interfacial phase transitions via combined experimental and theoretical studies. This is important because grain boundary phase behaviors can result in abrupt changes in transport, mechanical and physical properties. In the theoretical thrust, a thermodynamic model is developed for coupled adsorption and disordering transitions at grain boundaries by combining diffuse-interface and lattice-gas models and incorporating colloidal type interfacial forces. This model produces a systematical spectrum of interfacial phenomena for grain boundaries, including first-order and continuous coupled prewetting and premelting transitions, critical points, multilayer adsorption, layering and roughening, and complete wetting and drying; and it produces a series of discrete grain boundary phases. It is further demonstrated that the presence of dispersion and electrostatic forces in ceramic materials can appreciably change the grain boundary phase behaviors. Further refinements of the above phenomenological model lead to more realistic interfacial thermodynamic models that can be used to explain recent experimental observations of Si-Au and TiO_2-CuO-(SiO_2) systems. In the experimental thrust, a notable recent study (conducted in collaboration with Lehigh University, whose efforts are also supported by the same DOE-BES program) revealed a grain-boundary "phase" transition from a bilayer to an intrinsic (nominally clean) boundary in Si-Au. An atomically-abrupt transition between the two complexions implies the occurrence of a first-order interfacial phase transition associated with a discontinuity in the interfacial excess. This transition is unique in that the monolayer complexion is absent, which can be well explained by the theoretical framework developed in this project. In addition to the primary model system Si, grain boundary phase behaviors in several other materials systems have also been investigated experimentally. Although doped Si is selected as a proof-of-principle system, this model system is also technologically important because of the increasing usage of solar-grade polycrystalline Si. More recent studies have been conducted to investigate the surface phase behaviors of TiO_2 nanoparticles. This investigation is motivated by a critical need to establish a surface-grain boundary analogy to fill a fundamental knowledge gap in high-temperature interfacial thermodynamics, as well as the possibility to validate a potentially-transformative approach to improve the properties of photocatalysts and photovoltaic materials using interfacial phases.

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

Solid-state data storage systems are becoming ubiquitous for applications ranging from mobile devices, to laptop computers, to storage class media. However, substantial challenges exist for next-generation materials in terms of scalability, switching speed, reliability, and energy consumption. To investigate the fundamental mechanisms responsible for this behavior, High Speed Scanning Probe Microscopy (HSSPM) is employed for nanoscale property measurements of ferroelectric and phase change memory materials. Specifically, multiferroic films of $BiFeO_3$ are investigated to monitor the switching speed, nucleation time and site density, and local growth velocities, particularly focused on how these properties are influenced by microstructural constraints and/or defects. With GeSbTe phase change films, optical and electrically induced switching sites are characterized again in order to elucidate the switching mechanisms. Variable temperature studies are also underway. Based on these results, the data storage materials as well as the switching protocols are being engineered for optimal performance in terms of speed and energy consumption.

Transport and Imaging of Mesoscopic Phenomena in Single and Bilayer Graphene

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Funding:	$400,000

During FY 2011 we have made good progress in three areas: (1) imaging of fractional quantum Hall effect in graphene, (2) spectroscopy of ultra-high quality graphene devices on hexagonal boron nitride, and (3) fabrication of high quality graphene superconducting devices, both on hBN substrates and suspended. In area 1, we have been able to observe fractional quantum Hall effect in suspended graphene with factions denominators as high as 9. We are presently extracting the energy gaps for each of the fractions and exploring their spatial dependence. In area 2, we have investigated electronic transport in dual-gated twisted bilayer graphene. Despite the sub-nanometer proximity between the layers, we have identified independent contributions to the magnetoresistance from the graphene Landau level spectrum of each layer. We have demonstrated that the filling factor of each layer can be independently controlled via the dual gates, which we used to induce Landau level crossings between the layers. By analyzing the gate dependence of the Landau level crossings, we characterized the finite inter-layer screening and extracted the capacitance between the atomically-spaced layers. At zero filling factor, we observed magnetic and displacement field dependent insulating states, which indicate the presence of counter-propagating edge states with inter-layer coupling. This work was a result of a strong collaboration between the two PIs, and it is under review. In area (3), we have developed a new method to fabricate suspended superconducting graphene devices as well as on hBN substrates. This enables the measurement of the graphene transport characteristics in the presence of superconducting correlations, and more importantly, under conditions of reduced disorder. We are currently working on various mechanisms for ballistic Cooper pair injection on graphene and studying the interplay between superconducting phenomena (such as Josephson effect and Andreev reflection) and relativistic-like electron dynamics.

Atom Chip Microscopy: A Novel Probe for Strongly Correlated Materials

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Funding:	$255,000

Improved measurements of strongly correlated systems will enable the predicative design of the next generation of supermaterials. In this program, we are harnessing recent advances in the quantum manipulation of ultracold atomic gases to expand our ability to probe these technologically important materials in heretofore unexplored regions of temperature, resolution, and sensitivity parameter space. We are working to demonstrate the use of atom chips to enable single-shot, large area detection of magnetic flux at the 10^-7 flux quantum level and below. By harnessing the extreme sensitivity of atomic clocks and Bose-Einstein condensates (BECs) to external perturbations, the cryogenic atom chip technology developed here will provide a magnetic flux detection capability that surpasses other techniques—such as scanning SQUIDs—by a factor of 10-1000. We are testing the utility of this technique by using rubidium BECs to image the magnetic fields emanating from charge transport and magnetic domain percolation in strongly correlated materials as they undergo temperature-tuned metal-to-insulator phase transitions.

Electron Nanocrystallography of Complex Materials and Processes

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Electrons have large scattering cross sections, and electron beams can be focused using magnetic lenses. However, to use the full potential of electron beams for quantitative structural determination at the nanoscale, novel techniques must be developed to take advantage of coherent diffraction and newly developed ultrafast electron diffraction (UED). The scope of the proposed research is thus 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 includes the determination of 3D structure of selected Au, CdS and diamond nanoparticles, the determination of the symmetry and strain in nanometer-sized ferroelectric domains in relaxor ferroelectrics, as well as the determination of domain switching dynamics.

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 the discovery and control of optimal domain structure for electrical and mechanical coupling and sensing.

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

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Electron micrographs represent the image of the three-dimensional internal structure as it is projected on the electron exit side of the specimen. Consequently, in these projected two-dimensional images information along the beam direction is lost. This can result in incorrect interpretation of reactions. Furthermore, micrographs are snapshots in time of the evolution of the microstructure, the pathway often being suggested through a *posteriori* analysis. This project seeks to address both of these issues through using electron tomography for defect analysis to recover the lost information and to couple tomography with in-situ dynamic experiments to determine the reactions and pathways by which the microstructure is developed. The ultimate goal is to move toward four-dimensional characterization in which the dynamic experiments in the microscope are periodically interrupted to acquire the requisite number of images from which to construct an electron tomogram.

To create a successful tomogram requires acquiring images every degree over an angular tilt range of 140° with uniform contrast maintained across all images. These are demanding requirements for defect analysis, which often employ diffraction contrast imaging conditions. Recent progress includes the reduction in the angular tilt range and the number of images required to form a usable electron tomogram. This has been achieved by using the tomogram as the basis for constructing a traced model, which utilizes prior knowledge about dislocations and dislocation images to recover missing information. For metals with face-centered cubic crystal structures, the challenge of inserting the real space coordinate system in the tomogram and model has been solved. A solution to needing images acquired with diffraction vectors to reveal all defects has been resolved and tomograms with all defects present have been constructed. The remaining challenges are to reduce the number of images needed to form a tomogram, to allow noisy images to be used in the reconstruction, and to develop a family of algorithms specifically for this application as opposed to using components from multiple sources. The first two challenges must be addressed if this new technique is to be coupled with in-situ experiments as we move towards four-dimensional characterization.

This coupling of electron tomography with in-situ experiments is being used to explore microstructural evolution during deformation and how deformation modes, slip, and twinning, interact with obstacles such as other dislocations, precipitates, and interfaces.

In-Situ TEM Observations of Degradation Mechanisms in Lithium-Ion Batteries

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Funding:	$150,000

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. 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. However, without direct in-situ observation of these degradation mechanisms, with high spatial and temporal resolution, it remains difficult to understand and predict how these processes initiate, propagate, and interact. This research will 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. This project aims to 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.

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

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Funding:	$500,000

Processing under extreme environments presents unique challenges and opportunities for controlling the microstructure and thus properties of materials. Our research program emphasizes 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. Nanostructured 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 exploit self-propagating exothermic reactions in multilayers to achieve heating rates of up to 10,000,000 K/s, in addition to homogeneous thermal combustion reactions at more moderate rates (up to 100,000 K/s). These conditions place stringent demands on the experimental techniques. We use a combination of time-resolved x-ray microdiffraction, 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 are 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) are used to generate thermodynamic and kinetic parameters as inputs to the continuum models, which will in turn allow predictions (of reaction velocity, for instance) which 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 is done by using molecular dynamics 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. The effect of rapid heating and steep composition gradients on these phenomena is relevant to many systems of technological interest; highly exothermic reactions in multilayers happen to provide a convenient and experimentally tractable setting for exploring them.

Measuring Complementary Electronics Structure Properties of Both Deposited and Gas Phase Clusters by using STM, UPS, and PES

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Funding:	$167,000

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 these 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. Recently, we investigated (1) the surface morphologies resulting from the deposition of Mo100 versus $(MoO_3)67$ clusters by using STM and AFM imaging; (2) the ion-induced modification of small, size-selected, deposited metal oxide clusters by using AFM imaging and XPS; (3) the mobility of metal oxide clusters as a function of their cluster size by using AFM imaging; (4) the structural evolution of lead sulfide “baby crystal” cuboids on their way toward forming the bulk crystal structure by using STM imaging and XPS; and (5) the observation of novel fractal patterns due to the deposition of partially oxidized, titanium nitride clusters by using AFM. In our quest for mimics of precious metal catalysts and of rare earth-containing materials, we needed to determine the electronic structures of the species that we want to deposit on surfaces. For this, anion photoelectron spectroscopy has been utilized to provide electronic structure information about the cluster anions' neutral counterpart.

Discovering the Role of Grain Boundary Complexions in Materials

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This research program is focused on verifying the existence of grain boundary interfacial phases (complexions) in a range of materials systems, and characterizing their structures and range of stability. Complexions are atomic-scale equilibrium phases whose structure, chemistry, and stability are determined by thermodynamic parameters in a manner similar to bulk phases. Their distinguishing characteristic is that they are interface-stabilized and therefore may exist only at interfacial boundaries. This research program is a follow up of a breakthrough experimental study on the grain growth kinetics of alumina that – with the aid of aberration-corrected scanning transmission electron microscopy (STEM) – revealed the presence of six different complexions in alumina-based materials. These complexions were observed to exist as a function of chemical potential, temperature, and grain boundary crystallography including monolayer (submonolayer) adsorption, intrinsic-like behavior (a "clean" grain boundary), a bilayer, a trilayer, a nanoscale intergranular film (IGF) of equilibrium thickness, and a wetting film of arbitrary thickness. In the present research program, we have discovered similar grain boundary complexions in several new materials systems including Si-Au, TiO_2-CuO, Y_2O_3-(Ca, Si), and $SrTiO_3$ (the primary phases are underlined; the secondary phase is the dopant material).

Emerging Functionality in Transition-Metal Compounds Driven by Spatial Confinement

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Funding: $380,000

The exotic properties displayed by correlated electronic materials (CEMs) such as the cuprates, manganites, ruthenates, Fe-based penictides, and heavy-fermion compounds are intimately related to the coexistence of com¬peting nearly degenerate states which couple simultaneously active degrees of freedom—charge, lattice, orbital, and spin states. The striking phenomenon associated with these materials is due in large part to spatial electronic inhomogeneities, or nanoscale phase separation. In many of these hard materials, the functionality is a result of the soft electronic component that leads to self-organization. The challenge is to understand how such collective phenomena emerge. Spatial confinement on the length scale of the inherent phase separation can provide a window to probe the basic physics and reveal new emergent behavior. This project focuses on the exploration of novel behavior induced by spatial confinement and chemical or physical modification of the surface or interface. Thin films are grown and characterized in an ultra high vacuum environment. Lithographic techniques are utilized to form thin wires with dimensions on the scale of the characteristic phase separation, and the surfaces are modified in a controlled fashion to modify the functionality. The electronic and magnetic properties can be tuned in these spatially confined films by depositing electronic donors or acceptors, or by patterning of magnetic nano-clusters. Strain also gives a non-thermal parameter to be used to tune electronic or magnetic phase transitions. In essence, we are combining two of the Grand Challanges of the 21st century, complexity and nano-structured materials, to explore and exploit emergent behavior.

Imaging of Buried Nanoscale Optically Active Materials

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Funding:	$138,000

The project goal was to demonstrate and use Ballistic Electron Emission Luminescence microscopy to image the deeply-buried luminescent layer of semiconductor light-emitting devices with local hot electron injection from a Scanning Tunneling Microscope (STM) probe. Briefly, hot electrons are ballistically injected over a rectifying Schottky barrier into a n-i-p LED under bias. Electroluminescence from the optically active region directly below the injection point results from radiative recombination of these injected carriers. Microscopy is possible by raster-scanning the tip position.

Interfacial Thermal Resistance of Carbon Nanotubes

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Funding:	$138,000

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 it. 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.

Dynamical Nanoscale Crystallography with Femtosecond Resolution

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Funding:	$200,000

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. The advancement of ultrafast electron electron nanocrystallography (UEnC) is one way towards this ultimate goal. Employing femtosecond electron pulses and laser pulses in a pump-probe paradigm, it is possible to reconstruct the transient atomic structures by way of modeling the coherent electron diffraction pattern from optically excited nanostructures on the femtosecond timescale. In this proposal, we would like to pursue two directions of great 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, known as optical induced phase transitions (PIPT). These PIPT phenomena are considered to be gateways to explore the hidden states of matter far from equilibrium, and thus hold a special promise to elucidate the exotic phase of matter, such as high temperature superconductor. For the latter, we will conduct spatiotemporally resolved electronic and thermal transport measurements in nanostructures with our nano-probe setup to understand some of the peculiar phenomena that are thought to be intrinsic to nanoscale confinement, including nanofluids. These mechanisms are generally difficult to investigate 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.

Determining the Origins of Electronic States in Semiconductor Nanostructures

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Funding:	$155,000

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 (magnetic and non-magnetic) 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.

During 2011, we have published five papers, including two invited review articles.

Structure and Dynamics of Domains in Ferroelectric Nanostructures

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Funding:	$175,000

The main objective of the proposed research is to explore the fundamental nature of ferroelectric domains in strained ferroelectric thin films and fabricated nanostructures by advanced transmission electron microscopy (TEM) techniques in close collaboration with phase field modeling. The experimental techniques to be used include atomic resolution transmission electron microscopy and in-situ TEM using a novel scanning tunneling microscopy holder for TEM which allows the direct observation of nucleation and dynamic evolution of ferroelectric domains under an 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 artificially nanofabricated islands, and to understand the roles of crystal defects such as dislocations and interfaces in these processes; and (3) understand the physics of ferroelectric domain wall structure and properties (transport, band-gap, and dielectric response function), and the influence of defects (charged defects, dislocations, surface, and interfaces) on the basic structure and properties. The nucleation and dynamic evolution of ferroelectric domains observed by in-situ TEM under applied external electric field will be quantitatively analyzed and directly compared with phase field simulations. The theoretical modeling will be carried out based on experimental conditions including temperature, electric field, strain, and boundary conditions of TEM specimens.

The proposed work will provide a fundamental understanding of domain wall structure and properties and the roles of strain, electrical boundary conditions, and defects in the responses of ferroelectric thin films and nanostructures under an applied electric field. It will provide guidance for optimizing growth processes and creating nanostructures in novel devices. Although the proposed research focuses on $BiFeO_3$ thin films, the knowledge gained can be extended to similar materials such as multiferroics that undergo multiple ferroic phase transitions. The proposed research will also contribute to the development of human resources by training graduate and undergraduate students.

Study of Energy Transport at the Nanoscale

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Novel transport phenomena are expected to 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 and dissipation in MMMJs, the thermoelectric properties and spin dependent charge transport properties of MMMJs remains largely unexplored due to the lack of the required experimental tools. In order to achieve this goal, we are creating a novel instrument to probe heat transport in a variety of MMMJs and organic spin-valves. The proposed instrument combines (1) a high vacuum scanning probe and (2) an ultra-sensitive microdevice that can resolve heat currents with picowatt resolution. Using this technique, experiments will be conducted 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.

Nanoscale Resistive Switching Behavior of Ferroelectric and Multiferroic Tunnel Junctions

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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 is employed to study the critical and switching behavior in ultra-thin (several unit cells) heterostructures in conjunction with their transport properties. We use single-crystal epitaxial $BaTiO_3$ heterostructures 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 ferroelectric and multiferroic tunnel junctions (FTJs and MFTJs, respectively).

In FTJ, a writing pulse aligns the polarization and a subsequent current-voltage (I-V) measurements detect high or low resistance states depending on the writing pulse polarity. We investigate the properties of FTJ in $Au/Co/BaTiO_3/La_{2/3}Sr_{1/3}MnO_3$ heterosturctures grown on $NdGaO_3$ single-crystal substrates, which have 6 unit cells (u.c.) of $BaTiO_3$ (BTO). Giant tunnel electroresistance (TER) effect of more than 5×10^4 % is observed. The tunneling current at ON (low-resistance) state shows a remarkable writing pulse dependence as a longer pulse with higher voltage gave a higher tunneling current. However, the tunneling current at OFF (high-resistance) state shows no change with different writing pulses. The tunneling current at ON state decayed with time and the difference between ON and OFF states vanished within several seconds. Temperature dependence of the ON/OFF resistance states had been measured in the range from RT up to 150 ^{0}C. It is assumed that in our system, asymmetry of Co/BTO and BTO/$La_{2/3}Sr_{1/3}MnO_3$ interfaces might play an important role. Additionally, tunneling magnetoresistance (TMR) effect had been demonstrated at room temperature in the same heterostructures.

It is found that the main problem faced by the FTJs is the stability of polarization in ferroelectric tunnel barrier. We investigate polarization relaxation in $BaTiO_3$-based heterostructures by means of piezoresponse force microscopy (PFM) and pulsed switching current measurements (PUND). It is observed that although polarization is stable in ultrathin $BaTiO_3$ films with no top electrodes, deposition of top electrodes ($SrRuO_3$ or $La_{0.7}Sr_{0.3}MnO_3$) results in severe polarization relaxation. This effect is a consequence of strong effective depolarizing fields due to unfavorable interface terminations with the deposited electrodes, as opposed to more complete screening in the films by adsorbed charges on the free surface. Several approaches to enhance polarization retention in the case of a deposited electrode, including strain engineering and control of electrically boundary conditions have been explored. First-principle calculations based on density functional theory show that engineering of the atomic termination at the electrode interface with $BaTiO_3$ by insertion of ultrathin dielectric layers of $SrTiO_3$ can alleviate stability issues in the case of $SrRuO_3$ electrodes. Validity of this approach is experimentally confirmed by PFM observations and local PFM spectroscopy.

Nanoscale Properties of Novel Materials

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It is proposed to use a combination of nanostructure fabrication and multi-mode scanning probe techniques to investigate the properties of high-quality epitaxial thin films of two new systems of materials. The first system is the ferropnictides, a new class of high-temperature superconductor that has generated much interest in the last two years. The excitement over these new materials stems from the fascinating new physics that they might represent. While the ferropnictides share many properties in common with the cuprate superconductors, there are some fundamental differences. In particular, in the cuprates, the superconducting gap is anisotropic and originates from a single band at the Fermi surface, while in the ferropnictides, superconductivity is thought to arise from a multiband model involving different electron and hole Fermi surfaces. It has been predicted that this gives rise to a novel s+/- symmetry of the superconducting order parameter, but experimental evidence for this symmetry is still inconclusive. A major part of this proposal is devoted to experiments to elucidate the origin of superconductivity in these materials, with the unique aspect of the proposed work being the focus on experiments on high-quality epitaxial thin films of the 122 ferropnictides synthesized in Chang-Beom Eom's group at UW-Madison. Such films are available from only a few groups around the world. The availability of these epitaxial thin films combined with nanoscale fabrication and scanning probe techniques will enable the execution of experiments that are difficult or even impossible with bulk samples.

The second material that we propose to study is the conducting two-dimensional electron gas that is formed at the interface between two insulating perovskites, lanthanum aluminum oxide (LAO) and strontium titanate (STO), a unique system that was discovered only recently. Due to the strong electron correlations that exist in the complex oxides, this system promises to be a trove of rich new physics, particularly since the lateral dimensions of the resulting two dimensional electron gases can be reduced to the nanoscale using conventional nanolithography and scanning probe techniques, which we are well equipped to perform. The devices will be characterized by electrical magnetotransport and scanning probe microscopy techniques at temperatures down to the millikelvin range in order to explore the novel phenomena that are expected.

Epitaxial thin films of the materials to be investigated in this project will be synthesized in Eom's group at the University of Wisconsin-Madison, where they have recently been successful in producing epitaxial thin films of the superconducting ferropnictide $Ba(Fe_{1-x}Co_{x)}2As_2$ and LAO/STO epitaxial multilayers. Chandrasekhar's group at Northwestern will pattern devices using electron-beam lithography, and characterize them down to millikelvin temperatures using electrical transport measurements and scanning probe techniques, including atomic force microscopy (AFM), electrostatic force microscopy (EFM), point contact spectroscopy (PCS), magnetic force microscopy (MFM) and scanning tunneling microscopy (STM).

In addition to the training of graduate students and post-doctoral fellows, the research effort in the PI's group has had a strong history of participation by undergraduates and high-school students. This involvement will continue under this proposal with the initiation of a new outreach program to local high-schools involving laboratory visits and research internships, which it is hoped will increase the possibility of these students taking up careers in the `hard' sciences.

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

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Exploiting the spin degree of freedom of the electron offers new and powerful opportunities for enhancing the capabilities and performance of information processing systems. About half of the productivity growth in the U.S. economy is now attributed to information technology. The exponential growth of the electronics and semiconductor technologies sectors of the economy foretell unsustainable growth in energy consumption associated with these essential technologies absent significant shifts in approach. It is essential to develop information processing technologies that generate less waste heat and consume less energy.

Exchange bias plays a central role in information storage through its role in giant magnetoresistance magnetic field sensors employed in high density disk drive read heads. However understanding of the detailed mechanisms by which exchange bias couples to and pins the magnetization of an adjacent ferromagnetic layer remain incomplete. This is due in part to the complicating fact that observed behavior represents the spatial average over a nonuniform interfacial layer of the antiferromagnet leading to complex and poorly understood behavior.

Spin waves have been used to transmit information at gigahertz frequencies and for logic operations. These demonstrations of spin wave based logic and communication indicates an attractive approach to information processing and logic that avoids charge transport with its attendant power dissipation.

There is a pressing need for spatially resolved probes of exchange bias fields and magnetic properties in order to unravel the complex phenomena occurring at the buried antiferromagnet/ferromagnet interface at the heart of exchange bias systems. As spin devices become smaller to enable large scale applications, microscopic imaging of spin wave phenomena including interactions with the local fields used to manipulate the spin waves will also be essential.

We have demonstrated a novel technique, Ferromagnetic Resonance Imaging (FMRI) [Nature, vol. 466, p 845--848 (2010)], which microscopically probes static and dynamic magnetic properties of buried ferromagnetic structures and interfaces. The intense, spatially confined magnetic field of the micromagnetic probe tip mounted on a cantilever localizes the FMR mode immediately under the probe. With this microscope we have demonstrated imaging in ferromagnets with 200 nm spatial resolution and 1 Gauss/sqrt Hz field resolution in nanoscale volumes. Straightforward improvements of this approach will allow this dimension to be decreased to tens of nanometers. This important advance will enable new approaches to understanding exchange bias and magnetization dynamics.

We are using the microscopic imaging capabilities of FMRI to study exchange bias systems and spin wave properties in patterned films. In particular, we are mapping the interfacial exchange coupling between an exchange bias antiferromagnet and an adjacent ferromagnet and exploring intentionally introduced spatial variation of the exchange bias field and map the microscopic, naturally occurring, variation of exchange bias field in exchange bias systems. Spin wave device functionality will rely on efficient mechanisms for manipulating spin waves. Experiments allowing microscopic studies of mechanisms for manipulating spin waves---localized magnetic fields and exchange bias---are under development.

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

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The first main objective of this project is to probe the fundamental electronic and magnetic properties of nitride-based material systems, and in particular, specific bi-layer systems consisting of atomic layers of magnetic materials deposited onto semiconducting nitride surfaces. These include ferromagnetic metals, magnetic nitrides, and dilute magnetic nitride semiconductors. Such spintronic systems hold high promise as advanced materials for future energy-related applications. The second main objective of this project is to develop a strong U.S. effort in spin-polarized scanning tunneling microscopy. Based on the high level of activity involving unique instrumentation and research methodology, the principal investigator (PI) is well-positioned to accomplish these two objectives.

The PI has a history of accomplishment in the nitride materials field, beginning with the first proper identification of the two important families of surface reconstructions which occur on the basal plane surfaces of wurtzite gallium nitride – the (0001) and (000-1) faces – using scanning tunneling microscopy in 1997-99. Since 1998 at Ohio University, the PI has developed a full-scale research program to explore the fundamental properties of diverse classes of nitride systems, including semiconducting, magnetic, and spintronic nitrides. Furthermore, the PI also began a research program in spin-polarized scanning tunneling microscopy, achieving atomic-scale magnetic resolution of the antiferromagnetic surface Mn_3N_2 (010) already by 2002. This led to a series of articles and motivated the current project.

This DOE project involves both synthesis and analysis of magnetic and spintronic nitride materials. The experimental approach involves (1) epitaxial growth of selected magnetic nitride systems using molecular beam epitaxy and/or pulsed laser epitaxy; and (2) investigation of these systems using in-situ scanning tunneling microscopy and spin-polarized scanning tunneling microscopy, as well as an array of additional characterization tools. Spin-polarized scanning tunneling microscopy is a uniquely powerful technique which measures the spin-polarized local density of states of a surface as well as the normal (non-spin-polarized) local density of states. By coupling this technique to a powerful growth facility via ultra-high vacuum, the intrinsic spin-polarization of a clean surface may be determined.

The work is carried out within the PI's two independent laboratories at Ohio University. The first laboratory is geared towards room-temperature, spin-polarized measurements under magnetic fields up to 1/2 Tesla, while the second is dedicated to low-temperature, spin-polarized measurements under magnetic fields up to 4.5 Tesla. This project is also enabling the PI to foster a strong and skilled research group involving graduate, undergraduate, and post-doctoral researchers.

This project will impact all possible magnetic and spintronic applications of nitrides. In each and every potential and promising application, it is essential to understand the fundamental nature of the spin-polarization of the magnetic/spintronic layer, down to the atomic scale, and in particular for thicknesses in the range 0-5 atomic monolayers. This is because of the critical nature of the magnetic states at the interface with the semiconductor. This DOE project addresses in a new way, long-standing questions about the origins of magnetism within dilute magnetic nitride semiconductors by atomically resolving the magnetic atoms and the spin states directly, and as a function of growth conditions. Finally, this project establishes a U.S. spin-polarized scanning tunneling microscopy research program capable of addressing challenging new problems in nanoscale magnetism and spintronics.

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

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This program is focused on investigating the domain structures and dynamics in ferroelectric thin films and nanostructures. The main objective is to fundamentally understand the electromechanical effects on ferroelectric domain stability and on mesoscale domain switching mechanisms. The primary material system to be studied is $BiFeO_3$3, 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 (3D) ferroelectric domain evolution with spatial distributions and transport of charged defects; (2) study the 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. The proposed theoretical research will be carried out in close collaborations with a number of experimental groups who use High Resolution Transmission Electron Microscopy (HRTEM), In Situ TEM with Scanning Probe Microscopy (SPM), or Piezoresponse Force Microscopy (PFM) to characterize the domain structures and dynamics in high-quality ferroelectric $BiFeO_3$ thin films.

Local Electronic and Dielectric Properties at Nanosized Interfaces

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Funding: $135,000

This research program aims to advance our understanding of size dependent properties of interfaces and local behavior of constrained defects. The objectives of this research are to develop new probes of local complex properties and to apply them to open questions regarding interface behavior that impact devices used in energy applications. Specifically, size dependent Schottky barriers and orientation dependent electronic structure have been observed from transport measurements on nanosized metal/oxide interfaces. The origin of the size dependence will be examined by quantifying the dependence over a larger size regime, by measuring the effect of the metal work function and by varying the oxide polarity. Single crystal $SrTiO_3$ (100) and ZnO (0001 and 1000) will be used as model substrates and Au and Pt will be used to produce the interfaces. Experimental measurements will be described in terms of the relevant classical and tunneling transport models. As an extension of our development of frequency dependent measurements such as nanoimpedance microscopy, a local version of deep level transient spectroscopy based on scanning probe microscopy will be developed to probe interfaces states, and a scanning probe based microwave frequency spectroscopy will be applied to the interfaces to compare orientation effects. These new local spectroscopies will also be applied to the characterization of defects in nm thick oxide films.

Understanding and controlling size dependent interface properties is prerequisite to successful implementation of devices with nanoscale components, such as Plasmon enhanced photovoltaics, piezoelectric energy harvesting devices, and miniaturization strategies for thermal, optical and electronic sensors. The new scanning probes will enable studies extending far beyond this project.

Electron Density Determination, Bonding and Properties of Tetragonal Ferromagnetic Intermetallics

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Ordered intermetallic phases offer unique properties, often superior to those of elemental metals and compositionally equivalent solid solution alloys, rendering them suitable for various high-performance applications. The properties of ordered intermetallics are related to their electronic structure. Establishing robust, accurate and commonly accessible methods for probing electronic charge density in crystalline solids remains a high impact goal of basic science. Motivated by recent considerable progress in understanding transition metal intermetallics properties from electronic structure calculations we use these chemically ordered phases as examples to investigate aspects of charge density determination by convergent-beam electron diffraction (CBED) in a transmission electron microscope. CBED permits study of nano-scale volumes, thereby offering access to a broad range of crystalline phases. Our experimental studies focus on charge density as one of the quantum mechanical characteristics central for developing fundamental understanding of material properties and for validation and improvement of electronic structure theory in solids. Previous application of CBED to transition metal based intermetallics suffered from uncertainties in Debye-Waller (DW) factor measurements, which are considered essential for electronic structure determination. DW factors are known for most stable elemental crystals. However, intermetallic bonding can alter them significantly. We developed a robust experimental CBED method for the simultaneous measurements of multiple structure factors and DW factors in intermetallics and subsequent determination of electron charge density maps. Relative to solids comprised of light elements (e.g., $Z=14$, where Z is the atomic number), experimental bonding studies in intermetallics based on d-electron transition metals are very challenging due to increasingly stringent requirements for the precision on structure factor measurements. Quantitative CBED experiments promise an additional and effective path towards validation of electronic structure theory and further progress on understanding electronic structure – properties relationship in intermetallics.

The main objective of the effort is the development and application of quantitative convergent-beam electron diffraction (QCBED) methods for electron density and bonding electron charge density distribution determination in binary intermetallics involving d-electron transition metals. We use the FePd and FePt based L10-phases as model systems for comparative investigations of 3d-4d and 3d-5d systems. Furthermore, we include the non-magnetic iso-structural L10-phase TiAl to assess possible effects from the ferromagnetism. For FePd and TiAl binaries of equiatomic comosition comparison of experimentally determined charge density with results from DFT calculations using different approximations (e.g., mean-field approximation, LDA, and beyond-LDA all-electron calculation) are in progress. In the future, direct comparisons of FePd (3d-4d) and FePt (3d-5d) and effects of compositional deviations from the equiatomic, e.g., Pd-rich in FePd, on the electronic structures of the intermetallics will be addressed. The quantitative experimentation by CBED using energy-filtered transmission electron microscopy instruments delivers data sets, e.g., structure factors, electron density distribution and charge difference maps, suitable for direct comparison with equivalent metrics determined by density functional theory based calculation. Thereby, this effort will facilitate improved validation of results from DFT models and assist development of improved solid-state theory.

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

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PROJECT OVERVIEW

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.

PROGRESS

The error in such magnetic field measurements is commonly improved by noise averaging the signal through increased measurement time. However, the best precision typically requires restricting the maximum possible field strength (Bmax) to be much less than the sensor's spectral linewidth; or else a trade-off with the precision occurs, necessitated by increasing the measurement bandwidth and thus reducing the signal to noise ratio. Quantum effects such as entanglement and squeezing usually improve the precision only in the first scenario, and they are difficult to achieve in practice, especially in solid-state environments. We have implemented novel phase estimation algorithms on a single electronic spin associated with the nitrogen-vacancy (NV) defect center in diamond to achieve ~ 8.5x improvement compared to standard measurements, over a field sensing range ~ +/- 0.3 mT that is large compared to the spectral linewidth. The field uncertainty in our approach now scales as 1/T^0.88, in contrast to the standard measurement scaling of 1/T^0.5. Besides their direct impact on magnetic sensing and imaging at the nanoscale, these results open the way for quantum control and feedback techniques to be applied to sensitive magnetometry applications. This work has now been accepted for publication in Nature Nanotechnology.

This project currently supports one postdoctoral fellow, Ummal Momeen and one graduate student, Naufer Nusran.

Electron Mapping on the Nanoscale

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HIGH-RESOLUTION PHOTOEMISSION ELECTRON MICROSCOPY

Photoemission electron microscopy (PEEM) is a unique microscopy method which is currently in extensive use in magnetism, surface science and ultra-fast microscopy. The striking feature of PEEM is that it combines photon probing with electron imaging. In PEEM the imaging electrons originate from a photoemission process when the specimen is exposed to ultra-violet or x-ray light. The photoelectrons are subsequently accelerated and introduced into an electron-optical system to produce an image. This way of preparing the imaging electrons is much gentler than the use of electron beams – an advantage that becomes significant when fragile organic or biological structures are to be studied. Other unique advantages in PEEM are its high surface sensitivity, which allows a probing of nanovolumes without extensive sample preparation, and the unique surface contrast in PEEM which can be chemical, electrical or optical in nature. Finally, PEEM allows a large arsenal of photon-based spectroscopies to be implemented, among them ultra-fast methods.

In the past years our research group has designed and built an aberration-corrected photoemission microscope which now has the highest spatial resolution available. We propose to bring the resolution of this unique instrument from its current value of ~5nm towards 2nm. The feasibility of this ultimate improvement is confirmed in our recent experimental and theoretical results. Concurrent with the instrument development we will carry out new work on characterizing and utilizing localized surface plasmons as nanoscale light sources in microscopy. We will first visualize and characterize this type of plasmon in nanostructured metal films using femtosecond light pulses in PEEM, and subsequently optimize the plasmon generating structures for strong enhancement of localized optical fields. The optimized structures will then be used as nanoscale light sources in the study of semiconductor quantum dots and biological protein structures. Optical absorption and excitation as well as hot-carrier transfer effects will be studied. In the organic materials we will focus on utilizing localized plasmons for labeling and for light-activated chemical modification, taking approaches in close analogy to all-light-optical microscopy techniques.

The scientific merit of this project lies in the significant enhancement of resolution in PEEM and, in fact, in all photon-based microscopies, and in combining this resolution with the versatility of nanoscale illumination, labeling and light-activated chemical modification.

Probing Correlated Superconductors and their Phase Transitions on the Nanometer Scale

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Physics of High-Tc Cuprates Superconductors—*Nature* (2010): Our team focused on understanding the light hole doped cuprates in order to understand how high-Tc superconductivity emerges from a Mott insulating state. Building on our past experiments (Gomes et al. *Nature* 2007, Pasupathy et al. Science 2008) we produced two more important findings in this area. First, we showed that that the pairing interaction in underdoped samples (close to the Mott insulating ground state) is saturated in strength and the portion of the Fermi surface participating in the pairing interaction controls the superconducting transition temperature (Pushp et. al. *Science* 2009). The d-wave superconductivity emerges from the electronic state in a specific part of the Fermi surface while the rest of the Fermi surface exhibits so-called pseudogap behavior which competes with superconductivity. Second, (Parker et al. *Nature* 2010), we showed that the onset of pseudogap behavior (a precursor to superconductivity) coincides with the appearance of real space electronic modulations that have predicted characteristics of fluctuating stripes. These experiments, the first to isolate the interplay between the formation of stripes and pseudogap behavior in cuprates show that the pseudogap state is inherently unstable to make real space patterns of spin and charge that fluctuate.

Visualizing Kondo Lattice & Unusual Electronic Behavior of Heavy Fermion Systems—PNAS (2010): In compounds with partially filled f orbitals, electronic excitations act as heavy fermions. Several of the heavy fermion compounds display competition between magnetism and superconductivity and have a propensity toward superconducting pairing with unconventional symmetry. We successfully applied STM techniques to the study of these systems. We provided a local perspective of Kondo lattice behavior in these compounds and showed how this behavior is connected with novel electronic organization in these compounds, such as the “hidden order” phase that forms in URu_2Si_2. Currently no other experimental group has the STM capabilities to perform high-resolution experiments across the wide range of temperatures we can study. Our experiments complement the scattering and ARPES studies also supported under the DOE-BES program.

Topological Surface State—*Nature* (2010): DOE-BES partially supported these projects by supporting infrastructure at Princeton Nanoscale Microscopy Laboratory (support noted in publications). Topological insulators have unusual conducting surface states with Dirac-like energy dispersion and helical spin texture. Our group was demonstrated that these states are protected from backscattering due to their unusual spin texture. (Roushan et al. *Nature* 2009) We demonstrated that not only do these surfaces not back scatter but they can penetrate through crystalline barriers that stop other surface states (Seo et al. *Nature* 2010). These breakthroughs demonstrate the novel properties of topological surfaces.

Visualizing Critical Fluctuation Near the Metal-Insulator Transitions—*Science* (2010): DOE-BES partially supported these projects by supporting infrastructure at Princeton Nanoscale Microscopy Laboratory (support noted in publications). While localization and metal-insulator transition are well-understood phenomena in the limit of weak interaction, its behavior in the interacting limit continues to be at the forefront of physics. Electronic states in disordered conductors that are on the verge of localization are predicted to exhibit critical spatial characteristics due to their proximity to a metal-insulator phase transition. We used scanning tunneling microscopy to visualize electronic states in Ga1-xMnxAs samples close to the metal-insulator transition and showed that their spatial variations are indicative of critical phenomena. (Richardella et al. *Scienc*e 2010) Near the Fermi energy, the electronic states exhibit a diverging spatial correlation length. Power-law decay of the spatial correlations is accompanied by log-normal distributions of the local density of states and multifractal spatial characteristics, similar to those predicted for localization of non-interacting electrons.

Discovery of Dielectric Response and Forces in Sub-Nanoscale Objects

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Funding:	$200,000

This project explores the dielectric response of nanoscale and molecular-sized objects, using an aloof sub-angstrom fast electron beam, to obtain detailed information for estimation of inter-object forces, the strength of near and far-field photonic coupling, and possible unanticipated optical behavior in molecular and nano-scale objects.

With the recent development of aberration corrected electron microscopy, we are able to obtain the structure of atomic clusters ranging from single atoms up to several nanometers in size. Several types of processes are observed: atomic-level movement among strong binding sites, transition with cluster size from molecular bonding with the substrate to metallic behavior, cluster rotation and structural transformations, and coalescence of clusters under influence of the electron beam.

We will explore atomic clusters of various kinds deposited on, or incorporated within, different types of thin substrates, including graphene. Electron Energy Loss Spectroscopy using Angstrom-level beams will obtain spatially resolved dielectric losses to compare with earlier results from larger, 5-10 nm sized systems. Calculations will be used to increase understanding of near- and far-field dielectric response, and to estimate resulting inter- and intra-object forces to decide if observed atomic-level movement under the electron beam can be understood within the standard dielectric theory.

A detailed understanding of dielectric response of nanoscale objects would contribute to many activities in materials physics, chemistry, and biology. Measurement of coupling to external electric fields in molecule-particle systems will facilitate detailed understanding of Surface Enhanced Raman Scattering. Estimation of inter-particle forces will enhance our understanding of van der Waals fluctuation forces in complicated shapes, and may therefore contribute to a better understanding of molecular self-assembly. Measurements of dielectric response in hybrid inorganic/organic systems and comparison with density functional theory optimized for sparse systems will aid understanding of collective effects in arrays of quantum confined objects and the far-field coupling of those systems with light. Measurements of resonant surface plasmon modes in metal/dye composite structures may provide information about surface plasmon amplification and stimulated plasmon emission. Observation of molecular configuration changes would aid understanding of photosynthesis in biological systems and may suggest strategies for design of light harvesting devices for future sources of energy. Finally, excitation of symmetric nanoscale metal structures under non-dipole conditions produced by the small impact parameter may provide information about surface plasmon mediated negative index of refraction, suggesting new methods for manipulating light at the nano-scale.

Vortex Matter in Confined Superconductors and Mesoscopic Hybrid Heterostructures

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Funding:	$205,000

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).

The task of the project is to identify new physical phenomena associated with the competition between spatial confinement, proximity effect and the presence of a local magnetic order, to investigate vortex matter in these systems and to correlate macroscopic transport properties with local electronic density of states.

The goal is to understand how the physics of vortex matter changes in order to be able to predict and control the electronic properties of new hybrid systems. To have a proper description of small superconducting systems and hybrid superconducting/ferromagnet heterostructures, one needs to know the quasi-particle density of states, which is strongly modified compared to bulk materials due to quantum interference effects. Scanning Probe Microscopy and Spectroscopy is an integral part of this study. The vortex configuration can be probed with high spatial resolution by mapping the spatial variations in the electronic density of states with Scanning Tunneling Microscopy (STM). The understanding of the local changes in the electronic density of states is crucial as it also affects all the thermodynamic properties of the material.

Understanding and exploring the rich variety of quantum effects in mesoscopic superconductors and S/F heterostructure will stimulate both theory and experiment in the area of nanoscale physics and has the potential to significantly contribute to the understanding of magnetic pinning effects for applications of superconductors.

Physics of Complex Materials Systems Through Theory and Microscopy/EELS

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Funding:	$257,000

The project's objective is the study of complex materials systems by combining first-principles density functional theory (DFT) calculations with Z-contrast images and electron-energy-loss spectroscopy (EELS) obtained by a scanning transmission electron microscope (funding is provided only for the theoretical part). The project is pursued using available theoretical methods and by developing new methodologies. More specifically, a primary objective is to develop the capability of including both diffraction theory and solid-state fine structure in EELS calculations. This capability has been lacking, but is necessary to extract information from probe-position-dependent EELS that are currently obtained with very high spatial resolution using aberration-corrected microscopes. An initial implementation of such methodology has been accomplished and has been applied to data in $LaMnO_3$ (post-doc Micah Prange working with co-PIs Pantelides and Oxley). Another methodological objective is to employ time-dependent density functional to implement diffraction theory as an alternative to the prevailing "mutltislice" methodology (post-doc J.-A. Yan working with co-PIs Varga and Pantelides). An initial implementation has been accomplished and demonstrated for Si thin films and graphene.

An example of combining theory and microscopy to probe the properties of complex materials systems is the recent work by Tim Pennycook, a graduate student funded by the grant. Tim performed finite-temperature DFT calculations to explain recent experiments that found colossal ionic conductivity in yttria-stabilized zirconia (YSZ) thin films sandwiched between strontium titanate (STO) layers. This system has potential applications in fuel cells. Tim demonstrated that the origin of the colossal ionic conductivity is an extreme disordering of the oxygen sublattice in the YSZ layer, originating from a built-in strain and a mismatch between the oxygen sublattices in YSZ and STO. He then used the microscope to demonstrate that the EELS spectra indeed reveal a disordered oxygen sublattice as predicted by the theory. In other work by post-doctoral fellow Jaekwang Lee, theory combined with microscopy explained why the battery-cathode material $LiFePO_4$ has one-dimensional Li channels that are not blocked by Fe antisite defects. It was found that Li vacancies bind to antisite defects with a small binding energy. By segregating antisite defects in a few channels, the Li vacancies shuttle back and forth between neighboring antisites and spend more time being bound, which lowers the energy of the system. Microscopy established the existence of antisite defects with a vacancy on either site, as predicted by theory. The results provide guidance to optimize the material properties.

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

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Funding:	$180,000

The objective of this research program is to discover the fundamental mechanisms and atomic level phenomenon's that can provide understanding of piezoelectric response in lead-free ferroelectrics. A systematic study of the polymorphic phase transitions, local domain and crystal structure and their effect on physical properties will be conducted. $(Na,K)NbO_3$ (KNN) polycrystalline ceramics, single crystals, thin films, and textured ceramic systems close to polymorphic phase boundaries (PPBs) will be used as the representative lead-free system. Environmental scanning electron microscopy (ESEM) will be used to determine the nucleation and growth phenomenon in textured ceramics. For comparative studies, $(Na1/2Bi1/2)TiO_3$ single crystals and films with composition close to morphotropic phase boundary (MPB) will also be investigated. Nanoscale domain structure and its ferroelectric response will be studied as a function of electric field, pressure and temperature to identify the volumetric and phase fraction changes in the PPB region and to determine the presence of (any) intermediate phenomenon.

One of the challenging issues confronted in this research program is to formulate the mechanism of domain engineering in the lead-free materials. High resolution transmission electron microscopy (HRTEM), polarized light microscopy (PLM) and scanning probe microscopy (SPM) will be used to determine how the polar nano-domain structures are changed in the vicinity of PPB and MPB. Combining these investigations with lattice imaging and Z-contrast will provide answers as to how the boundaries between polar nano-domains changes with x% BT, compositional substitutions by aliovalently atomic species on the A-site and B-site, and electrical history. Further it will allow understanding of the role of nano-scale domains and the twin boundaries between them, and their important role on apparent phase stability and macro-response. The atomic resolution, of these near single atom probes, offer an exciting approach to investigating how defects and polarization interact at the atomic and nanoscales. Important questions related to engineering phase stability and transformation pathways between bridging phases, and thus enhanced piezoelectricity in Pb-free materials, can be answered. The crystal structure in the oriented single crystals will be investigated under varying electric field and temperature conditions to identify the lattice parameters, and domain distributions for various crystallographic directions for understanding of the intrinsic anisotropic response. Symmetry relations, nature of the dipole moment, crystallography and orientation of polarization will be determined by using diffuse neutron and X-ray diffraction, Raman Spectroscopy and Birefingence Imaging Microscopy (BIM). Using this information, various related questions will be answered such as: how elastic compatibility amongst hierarchial domains can enhance effective piezoelectric properties, and how oxygen rotational modes might influence the phase transformational sequence and piezoelectric properties. The results from these studies will establish the link between the physical property in question and the way certain parameters change.

Intrinsic Properties of Correlated Materials Derived From Combined Nanoscale Transport and Ultrafast Spatio-Temporal Imaging Experiments

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Funding:	$398,000

The goal of this program is to study strongly correlated materials on the nanoscale. These materials typically have intrinsic domain structure with characteristic lengths scales of tens of nm to microns arising from long-range forces, either elastic, electric or magnetic, that compete with ordering and symmetry breaking such as in metal-insulator transitions, ferroelectricity and ferromagnetism. We apply a combination of electrical measurements and new scanning optical and photocurrent techniques to bulk crystals, homogeneous single-domain nanoscale samples, and micro-crystal-based devices that allow for independent control of uniaxial strain and temperature.

One side of the project is the construction of a unique scattering-scanning near-field optical microscopy (s-SNOM) system for measurements on the sub-domain scale in a controlled environment, in magnetic and electric fields, and at a variable temperature (20 - 500 K). This allows us to combine linear, nonlinear, and ultrafast optical spectroscopies to study and dynamically image metal-insulator transitions and coupled ferroic ordering in multiferroic and ferroelectric materials through dielectric optical conductivity contrast and the symmetry selectivity provided by tip-enhanced second harmonic generation (SHG) and nano-Raman crystallography via the tensor-based selection rules.

The other side is the development of a complementary, and also unique, variable-temperature system that combines time-resolved micro-spectroscopy with sensitive dc and transient transport measurements, with the addition of environmental vapor control and high magnetic field (9 Tesla). This adds the ability to perform ultrafast and nonlocal spatially resolved photocurrent measurements on the single-domain level, which can reveal the fundamental mechanisms underlying the optoelectronic response, with in-situ control of the oxygen and hydrogen partial pressures that are often highly influential on the properties of oxides and their interfaces, and at magnetic fields large enough to reach new quantum regimes.

Characterization of Dopant/Point Defect Complexes in Semiconductors by STEM

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Funding:	$220,000

This project focuses on characterizing and simulating defects in compound doped semiconductors, semiconductor devices, and semiconductor nanostructures. We have investigated p-type doping of ZnO using As and Sb, In composition fluctuations in InGaN light emitting diodes (LEDs), and the properties of Ga-doped ZnO as a transparent conducting oxide.

We have found that Sb-doped ZnO nanowires synthesized by Xudong Wang's group at UW are reliably p-type. Through a combination of aberration-corrected Z-contrast STEM imaging and density functional theory (DFT) simulations, we have identified a new mechanism leading to this p-type doping consisting of Sb-decorated head-to-head inversion domain boundaries. In ZnO thin films, Sb is incorporated in other defects and does not lead to p-type conduction. We have discovered a new impurity/point defect complex in As- and Sb-doped ZnO thin films using DFT and explored the dependence of As diffusion on doping level.

We have used aberration-corrected Z-contrast STEM at low dose to show that, contrary to the widely-accepted explanation for their high light conversion efficiency, there are no nanometer-scale lateral composition fluctuations within the quantum well of a high-efficiency InGaN LED. Instead, high efficiency is achieved by large scale well-width fluctuations.

We have combined electrical measurements and STEM data to elucidate the carrier scattering mechanisms in heavily Ga-doped ZnO, a candidate material to replace indium-tin oxide as a transparent conducting oxide, especially in GaN-based optoelectronic devices. Ga induces a charge in growth surface polarity from Zn to O, leading to a high concentration of inversion domain boundary defects, reducing the carrier mobility and the material's conductivity. This effect can be reversed by an oversupply of Zn to the growth surface, switching the polarity back, and resulting in high-quality material.

Finally, we have begun a collaboration with mathematicians Peter Binev and Wolfgang Dahmen on achieving high precision and accuracy in STEM by non-rigid registration then averaging of multiple STEM images of the same sample area.

Tailoring Magnetism in Epitaxial Graphene on SiC

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Funding:	$185,000

During FY2011, we have made significant progress towards the understanding of electronic and magnetic properties of epitaxial graphene/SiC. First, we have unveiled the origin behind the selective imaging of the complex electronic structure of epitaxial graphene on SiC(0001), using W tips functionalized by transition metal coating [PRB 84, 125425 (2011)], which was vital to our recent discovery of the atomic structure of the interfacial graphene layer that has eluded the community for decades [PRL 105, 085502 (2010)]. Also based on this unearthing of the warped graphene interfacial layer with periodic inclusions of pentagon-hexagon-heptagon, we have discovered a novel Si diffusion path for the growth of pit-free graphene on SiC(0001) [PRB xx, 005400 (2011)].

Second, following our earlier work on the formation of ridges on the graphene layer/SiC [Nanotech 20, 355701 (2009)], we have further studied the electronic properties of the one-dimensional nanowires and zero-dimensional quantum dots induced by the bending and buckling of the graphene layer using scanning tunneling spectroscopy. Our results reveal strain induced pseudo-magnetic fields greater than 200 T on these graphene nano-structures [manuscript in preparation].

Third, we have found that hydrogenation of the epitaxial graphene/SiC using Ar/H_2 plasma led to the formation of resonant scatters (e.g., H-vacancy defects), which cause both intra-valley and inter-valley scattering. By measuring the wavelength of intra-valley scattering as a function of bias voltage in the dI/dV imaging, we have determined the impact of these resonant scatters on electron transport in epitaxial graphene/SiC. Furthermore, we have demonstrated the controlled desorption of adsorbed hydrogen atoms using the electric field associated with an STM tip [manuscript in preparation].

Last but not least, we have achieved the nano-cutting of epitaxial graphene on SiC(0001) using Fe nanoparticle-assisted hydrogen etching in ultrahigh vacuum (UHV), and investigated the electronic properties of the resulting edges. By carrying out both graphene cutting and characterization in-situ, we have circumvented issues related to contamination that may introduce sporadic defects and/or impurities to the edges, allowing the study of the intrinsic electronic and magnetic properties of these graphene edges [manuscript in preparation].

DOE National Laboratories

Emergent Phenomena in Ferroic Nanostructures

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Funding: $2,387,000

The goal of this research program is to investigate novel and emergent properties of oxide thin films and nanostructures, with an emphasis on ferroelectric, ferromagnetic and multiferroic systems along with systems displaying novel transport behavior. The term ‘emergent’ is used here to describe the complex and sometimes unanticipated behavior that can be displayed by simple and complex oxides when combined in nanostructures. These emergent phenomena can be harnessed for a range of energy-related applications such as photovoltaic devices, thermoelectric energy harvesting systems, and low-power non-volatile memories. We intend to elucidate the chemical, microstructural and interfacial contributions to their novel behavior.

Firstly, we seek to understand how synthesis affects the properties of multiferroic oxide films. Secondly, we seek to understand the mechanisms by which film properties are modified in nanostructures, through effects such as size confinement (including lateral confinement), charge transfer and band structure modification. Thirdly, we are developing a full understanding of the dynamic response in multiferroic nanostructures, including the physics underlying ferroelectric domain behavior, and ferromagnetic magnetization reversal mechanisms in thin films and patterned oxide nanostructures. We are combining advanced materials synthesis, complementary in situ and ex situ microstructural characterization, and analysis of physical behavior, as well as computer simulation and theory to accomplish our research objectives. A particular emphasis of our research is the development and use of 3D analysis tools, such as electron tomography and piezoresponse force microscopy, and modeling to elucidate chemistry and domain structure at the nanoscale in three dimensions.

Spectroscopic Imaging STM for Complex Electronic Matter Studies

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Funding: $320,000

VISUALIZING THE CREATION OF HEAVY FERMIONS

Within a Kondo lattice, the strong hybridization between electrons localized in real space (r-space) and those delocalized in momentum-space (k-space) generates exotic electronic states called ‘heavy fermions’. In URu_2Si_2 we used spectroscopic imaging scanning tunnelling microscopy (SI-STM) to image the evolution of URu_2Si_2 electronic structure simultaneously in r-space and k-space. Heavy-quasiparticle interference imaging within this gap reveals its cause as the rapid splitting below To of a light k-space band into two new heavy fermion bands. This was the first direct visualization of a Kondo-screening many-body state in magnetic lattice and the first use of heavy quasiparticle interference to determine a heavy fermion band structure (both above and below EF). This combined capability to simultaneously visualize the r-space Fano lattice and the k-space heavy fermion structure opens a completely new experimental window onto the physics of multichannel Kondo lattices and heavy fermion physics, and has generated great interest worldwide.

VISUALIZING THE DESTRUCTION OF HEAVY FERMIONS

Replacing a magnetic atom by a spinless atom in a heavy fermion compound generates a quantum state often referred to as a 'Kondo-hole'. No experimental imaging had been achieved of the atomic-scale electronic structure of a Kondo-hole, or of their destructive impact on the hybridization process between conduction and localized electrons that generates the heavy fermion state. We recently reported the first visualization of the electronic structure at Kondo-holes created by substituting spinless Thorium atoms for magnetic Uranium atoms in the heavy-fermion system URu_2Si_2. At each Thorium atom, an electronic bound state is observed. Moreover, surrounding each Thorium atom we find the unusual modulations of hybridization strength recently predicted to occur at Kondo-holes (Figgins J, Morr DK (2011) *Phys Rev Le*tt 107:066401). Then, by introducing the 'hybridization gapmap' technique to heavy fermion studies, we discovered intense nanoscale heterogeneity of hybridization due to a combination of the randomness of Kondo-hole sites and the long-range nature of the hybridization oscillations. These observations provide new and direct insight into both the microscopic processes of heavy-fermion forming hybridization and the macroscopic effects of Kondo-hole doping. Long-standing theoretical predictions for the electronic structure of a Kondo-hole including the suppression of hybridization near the substitution-atom sites the disordered hybridization fluctuations generated by random Kondo-hole doping, that an impurity bound-state appears within hybridization gap and that hybridization oscillations exist are borne out directly by these experiments. This agreement between theory deductions from macroscopic experiments provides growing confidence in the ability to predict theoretically and to detect experimentally the atomic scale electronic structure and, perhaps more importantly, the consequent hybridization disorder generated by Kondo-holes. The combination of SI-STM techniques introduced here provides a powerful new approach for study of the r-space and k-space electronic structure of heavy fermion systems.

Studies of Nanoscale Structure and Structural Defects of Advanced Materials

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Funding:	$2,148,000

The overall goal of this program is to study the property-sensitive nanoscale structures and defects of technologically important materials, such as superconductors, multiferroics, and other energy-related materials, including thermoelectric and photovoltaic devices, and batteries. We develop and employ advanced quantitative electron-microscopy techniques, such as coherent diffraction, atomic imaging, atomically resolved spectroscopy, and electron-holography to study the materials' behavior. We particularly emphasize gaining a detailed understanding of their structure-property relationships, and knowing how to control and manipulate atomic structure and defects to optimize the 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 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.

The impact and progress of our program during FY 2011 includes, but is not limited to, unraveling how high-resolution imaging of precession-orbits of a vortex-core under resonance excitations uncovers the effects of spin-transfer torque for spin-based devices; by what means does the spatial distribution of temperature-dependent charge/orbital-ordered nanoclusters contribute to colossal magnetoresistance in manganites; in what way do atomic defects boost thermoelectric power in $(Ca_2CoO_3)0.62CoO_2$; how can the distribution of valence electrons alter the superconductivity of the Co doped $BaFe_2As_2$ superconductors; by what measure does a core-shell structure enhance the chemical reactivity of Pd-Pt catalysts; and, what is the optimized microstructure of new electrode materials that offer higher power and energy density, longer life, and safer lithium-ion batteries.

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

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Funding:	$500,000

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.

Soft Matter Electron Microscopy Program

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Funding: $750,000

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.

Fundamental Mechanisms of Transient States in Materials

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Funding: $1,002,000

We aim to develop a fundamental understanding of materials dynamics (from µs to ns) in systems where the required combination of spatial and temporal resolution can only be reached by the dynamic transmission electron microscope (DTEM). 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. Using the unique in-situ capabilities and the nanosecond time resolution of the DTEM, we seek to study complex transient phenomena associated with rapid processes in materials, such as the atomic level mechanisms and microstructural features for nucleation and growth associated with phase transformations in materials, specifically in martensite formation and crystallization reactions from the amorphous phase. We also will study the transient phase evolution in rapid solid-state reactions, such as those occurring in reactive multilayer foils (RMLF).

We have imaged the evolution of transient microstructures in RMLF, rapid crystallization of binary intermetallic glasses and single component amorphous Ge, and rapid solidification in Al. In the NiAl RMLF studies, we have identified film compositions that form transient cellular microstructures composed of liquid and solid NiAl intermetallic phases and those that do not. We have identified and quantified C-curve behavior in the crystallization of amorphous NiAl. 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. We have demonstrated the ability to acquire time resolved convergent beam electron diffraction patterns in the DTEM. We have also demonstrated the capability to induce the amorphous to crystalline transformation and reverse it when desired in phase change materials using pulsed laser heating in situ in the DTEM.

We are currently building 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 will be able to acquire up to 16 images that will make a short movie of the event. This will, for instance, enable the study of the microstructural evolution at the propagating reaction fronts in RMLF. This capability will also aid in the study of phase transformations, where we can track the position of the interface as a function of time and observe the nature and mechanisms involved with the interaction of the interface with microstructural features that will allow us to more effectively model phase transformation kinetics. Characterization of such strongly driven systems in the DTEM includes crystallization of amorphous NiTi and Ge, solidification of pure and alloy systems in a planar geometry, and reaction of energetic multilayer films. We will continue these studies and expand them to include related phase transformations, with particular emphasis on the stability of the moving interface between the phases present as the structure evolves. We have found oscillatory behavior at two of these interfaces—crystallization of amorphous Ge and reactive multilayers—the origins of which we will pursue. The morphological instability of rapidly solidifying metals and alloys in planar geometries and reactive multilayer films will also be investigated. Over the long term, we expect that our time resolved studies will have significant impact in materials science in advancing our understanding of mechanisms of a variety of transient phenomena. We anticipate in-situ analysis of materials properties and reactions on the nanometer and nanosecond scales that provide unique insights to fundamental catalytic processes.

Atomic Mechanisms of Metal Assisted Hydrogen Storage

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Funding:	$567,000

The goal of this project is to establish the scientific basis for designing the building blocks of carbon-based nanoporous adsorbents that enable synergistic metal-carbon interactions, leading to enhanced hydrogen uptake at near-ambient temperatures. Our results indicate that embedding transition metal catalysts within nanoporous carbons with controlled nanoscale structure and porosity results in enhanced H_2 adsorption. This appears to result from atomic-scale interactions between molecular H_2, metal particles, and carbon with proper nanostructures. Theoretical calculations demonstrate that uptake may be significantly increased if sufficient control of the structure can be attained. To optimize the design of such nanostructures, it is essential to develop atomistic models that realistically describe isotropic nanoporous carbons, and to gain fundamental understanding, at the atomic and molecular level, of hydrogen interactions with nanoporous carbons and metal-doped nanoporous carbons. We will focus on three specific aims: (1) modeling and characterization of medium-range order in partially amorphous - partially graphitic structures of nanoporous carbons, (2) understanding the mechanism of molecular activation of H_2 by metal particles, and (3) elucidation of the energetics and dynamics of hydrogen species confined in the molecular space of pure- and metal-doped nanoporous carbons. State-of-the-art neutron and x-ray (synchrotron) scattering, advanced computation, and high-resolution electron microscopy all contribute to achieving our research goals.

Probing Phase Transitions, Chem. Ractions, & Energy Transfer at the Atomic Scale: Multifunctional Imaging w/Combined Electron & Scanning Probe Mic

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Funding:	$744,000

Electrical bias-induced phase transitions and electrochemical reactions underpin a wide range of applications ranging from such global issues as energy generation, storage and conversion to fundamental science of order parameter-structure couplings. To achieve a microscopic understanding of the thermodynamics and kinetics of these processes, we need the capability to probe them in-situ, on a single-defect level. Here, we plan to develop experimental tools for seamless combination of high-resolution electron microscopy, electron energy loss spectroscopy (EELS) imaging, nanofabrication, and local scanning probe approaches, while also formulating new methodologies for data analysis and interpretation using synergistically coupled advanced theoretical methods. Using these tools, we will study energy transformations in systems with increasing levels of complexity: (A) purely electronic transfer at interfaces and single dopant atoms in oxide grain boundaries, interfaces, and nanowire junctions; (B) electrostatically-driven structural changes and phase transitions in ferroelectrics and antiferroelectrics; and (C) electrochemical processes involving mass transfer that occur on charge injection at solid interfaces of the ionic conductors. We will uncover mechanisms of these transformations on the nanometer, and ultimately, a single-atom and single-electron level. This will enable optimization of a broad range of energy and information technologies from fuel cells, supercapacitors, and batteries, to data storage and energy.

STEM Atomic Structure and Properties of Materials

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Funding: $2,588,000

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, two dimensional spectroscopic images are feasible, and atomic resolution can be achieved with accelerating voltages as low as 60 kV, avoiding most damage events in materials such as graphene, boron nitride and polymers. We have a historic opportunity therefore to explore the atomistic origins of materials properties. This program both develops new methodologies for applying these instrumental advances to materials, and applies them in collaboration with groups in ORNL and outside, to cutting edge materials issues in nanoscience, chemical sciences and especially to energy materials. Specifically we explore and define the limits to resolution, in three dimensions, and the sensitivity and precision for locating single impurity atoms and mapping electronic structure. Key issues of interface science and materials physics include the origin of the unique properties of artificially synthesized complex oxide superlattices, and structure/function correlations in battery materials, iron-based superconductors, monolayer graphene and boron nitride.

Correlated Materials - Synthesis and Physical Properties

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Funding: $1,582,000

Work in this project addresses the Grand Challange of understanding and harnessing emergent phenomena, as well as a number of “Basic Research Needs” areas for energy applications in the realm of quantum materials. In broad terms, we seek to understand how complex interactions in strongly correlated electron systems lead to emergent quantum behavior, including unconventional superconductivity, charge and spin ordered states, and non-Fermi liquid effects. We combine a range of techniques to address these questions, including crystal growth and characterization of novel materials (with a focus on magnetotransport properties - Fisher & Geballe), local electronic (Kapitulnik) and magnetic (Moler) measurements, and theory (Kivelson). In all cases, our focus is on understanding the fundamental factors determining the often complex electronic properties of these materials from both an experimental and a theoretical perspective. We work collaboratively on materials and questions of mutual interest, often together with PIs from other FWPs within SIMES.

Experimental Condensed Matter Physics

Institutions Receiving Grants

Artificially Structured Magnetic Materials	
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Funding:	$32,000

Our research was directed toward understanding magnetism at surfaces and interfaces in high-quality, well-characterized materials prepared by Molecular Beam Epitaxy (MBE) and sputtering. This work is divided into three areas: the main focus is an understanding of ultrathin Fe layers on GaAs, the second area is understanding spin phenomena in ferromagnetic layers on III-V and II-VI semiconductors, and the third area involves spin polarized neutron reflection (PNR) in collaboration with Dr. Michael Fitzsimmons' group at Los Alamos National Laboratory.

The interactions in low dimensional and patterned magnetic nanostructures are presently not well understood, but are of considerable fundamental and practical importance. Single-crystal MBE-grown nanodots hold considerable promise, and our research addressed this area. We fabricated suitable epitaxial materials by MBE and then conducted studies of their magnetic properties using Brillouin light scattering (BLS). Our effort was unique in three ways: (1) our structures were formed in epitaxial films; (2) our structures were extremely thin, on the order of only a few monolayers; and (3) our in situ BLS instrumentation gives us exceptional ability to determine the magnetic properties. For these studies we used in situ RHEED and LEED to verify the single crystal nature of the films, and BLS to measure saturation magnetization Ms, and the first- and second-order anisotropy constants Ku(1) and Ku(2).

We conducted an in-situ scanning tunneling microscopy (STM) study of the Fe microstructure for coverages near the superparamagnetic-to-ferromagnetic transition. In addition, we made in-situ BLS measurements at low temperature to study the superparamagnetic phase in detail. By correlating the STM data with BLS and diffraction we were able to extract information about these transitions and their relation to structure.

Focused Research Center in Correlated Electronic Materials

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Students: 6 Postdoctoral Fellow(s), 8 Graduate(s), 3 Undergraduate(s)
Funding: $250,000

This Single-Investigator and Small Group Research Grant commenced on 9/15/09. The grant supports the collaborations among theory and complimentary experimental efforts (STM, ARPES, and Optics) at Boston College in one of the DOE Grand Challange areas of correlated electron and complex materials. The team has a track record of synergetic collaborations in the field of high-Tc cuprate and iron-based superconductors, sodium cobaltates, and strontium ruthenates. From 2010 to 2011, these collaborative research activities have led to seven published papers, including two in *Nature Physics*, two in *Physical Review Letters*, and one in *Nature Communications*.

Recent research activities of the group have led to the observation of the three-dimensional (3D) superconducting gap function in optimally-doped iron-pnictide superconductors and the description of the measured gaps on all Fermi surfaces by a single 3D gap function that is consistent with the existence of only two dominate pairing energy scales, the in-plane and out-of-plane pairing strengths. This work points to a common origin for the pairing strength on all Fermi surfaces and provide the much needed insights for understanding the mechanism of superconductivity in Fe-based superconductors. The iron-pnictides are multiorbital systems where the electron correlation strength is intermediate and comparable to the kinetic energy. This intermediate interaction regime represents the challenge for understanding correlated systems as the electrons straddle between having predominantly itinerant and localized characters. The team’s theoretical work revealed that nonperturbative correlation effects are essential to stabilize the metallic spin density wave phase with small magnetic ordered moments observed experimentally. For the high-Tc cuprate superconductors, the combined STM and neutron scattering experiments on optimal electron-doped PLCCO samples demonstrated the spatial coexistence of superconductivity and antiferromagnetism. Contrary to phase separation observed in some hole-doped copper-oxides, the AF order and the superconductivity are found to be inhomogeneous and compete locally on nanometer scales in electron-doped materials. The group has also initiated research efforts in the field of topological insulators. Recently accomplished works include the observation of broken time-reversal symmetry using combined STM and ARPES probes on the surface of magnetically doped topological insulators; and the discovery by STM of unidirectional stripes and the induced periodic modulations in the Landau level energies that raise the potential to realize 1D quantum wires using topological insulators.

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

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Funding: $150,000

The scientific and technological interest in solid state conductivity transitions is enormous. The switching of the electrical properties of a material between those of a metal and those of a non-metal (be it semiconducting, semimetallic, insulating, or superconducting) is the very basis of the electronics industry. These transitions can be driven by many external and internal mechanisms, including, but not limited to, applied electric and magnetic fields, chemical doping, defects, disorder, pressure, and temperature. While the technological applications of such transitions are numerous, these transitions are also the focus of significant fundamental physical interest. Indeed a substantial fraction of all research in solid state physics is directed at understanding such transitions in some form or another, and almost every conceivable experimental technique has been applied in an attempt to identify their origin, and control their behavior.

Vanadium oxides are a class of solids that display particularly complex and fascinating properties. Whether as simple binary oxides or as ternary compounds with another metal cation, these oxides are replete with complex conductivity transitions, as well as charge ordering transitions, structural phase transitions, frustrated spin structures, superconductivity, and unusual magnetic properties. As such, vanadates are prototypical correlated materials, and allow important physical themes to be explored both experimentally and theoretically. Key to understanding the origin of all these phenomena in the vanadates is accurate experimental determination of the underlying electronic structure.

This program aims to make definitive spectroscopic measurements of the electronic properties of a selection of vanadium oxides. The primary goal is to use the knowledge 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, soft x-ray absorption spectroscopy, resonant inelastic soft x ray scattering, x-ray photoemission spectroscopy, and angle resolved photoemission spectroscopy. The use of this suite of techniques enables a wide range of oxides to be studied, since are able to measure electronic structure in electrical conductors and insulators, and samples in crystal, thin film, or powdered form.

During the current reporting period, we completed three vanadate studies: (a) measurement of orbital anisotropy and low-energy excitations of the quasi-one dimensional conductor ß-Sr0.17V2O5, (b) measurement of electronic structure in the ferromagnetic insulator V0.82Cr0.18O2, and (c) measurement of electronic structure in the photoelectrochemical water splitting oxide $BiVO_4$.

Thermal Transport in Correlated Low Dimensional Electrons Systems

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Funding:	$150,000

This project is underway at the California Institute of Technology under the scientific direction of Principal Investigator (PI) James P. Eisenstein. The PI and his research group consisting of graduate students and postdoctoral associates study the fundamental physical properties of 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 are 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.

We seek to answer fundamental questions about 2D electron systems. For example, we hope to determine whether the exotic “non-abelian quasiparticles” predicted by theory are really present in certain fractional quantum Hall states at high magnetic field. Proof of the existence of such objects would have important implications for physics and quantum information science. Our approach is based on the known connection between the entropy of an electron system and its thermoelectric power. Non-abelian quasiparticles are anticipated to possess an anomalously large entropy at low temperatures and this may be reflected in the thermopower.

Graphene represents another focus of our research. Our present aim is to study the electronic properties of suspended samples which contain only a few layers of carbon atoms (typically 1 to 3). Suspended systems are cleaner than samples on substrates and thus more likely to display subtle correlated electron phases. Multilayer samples are particularly promising owing to the large discrete degeneracy of their Landau level spectra. This degeneracy offers numerous prospects for spontaneously polarized (pseudo-ferromagnetic) phases.

Finally, we employ surface acoustic wave (SAW) techniques to explore two-dimensional electron systems. One planned application is to examine graphene deposited on GaAs, a piezoelectric semiconductor. SAWs on the GaAs will provide access to the conductivity of graphene at much shorter length scales than conventional transport measurements. We will use surface acoustic waves to examine the exotic Bose-Einstein condensate of excitons which appears in double layer 2D electron systems at high magnetic field. This unusual state, discovered in the PI’s lab with support from DOE, is at once closely related to superconductors and to ensembles of ultra-cold bosonic atoms.

Investigating the Role of Ferromagnetic Materials on the Casimir Force

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Here we propose the first experimental and complimentary theoretical study of the role of magnetic materials in the Casimir force. The role of the Casimir force has become recognized as central to the performance, function and fabrication of MEMS devices. 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. For simple planar geometries and dilute systems, the Casimir force can be viewed as an extrapolation of the van der Waals force to macroscopic objects and large separations. However in contrast to the van der Waals force the Casimir force can be both attractive and repulsive depending on the boundary geometry. The last ten years have seen increasing levels of sophisticated experiments, which have provided tremendous impetus to the development of a more solid theoretical foundation of the material dependences of the Casimir force. These rapid theoretical developments have raised fundamental questions on the role of material parameters which are the subject of many ongoing experiments. The material parameters investigated have already opened many promising avenues for technological applications. This provides urgency to the investigation of the material properties that are still unexplored with regards to the Casimir effect.

At present there is no experiment based understanding of the role of magnetic materials in the Casimir force. Previously, it was thought that two strongly ferromagnetic materials would overwhelm the Casimir force. The effect was thought to be negligible if only soft magnetic surfaces were used. Contrary to these assumptions, we show through preliminary calculations, that the magnetic materials might have subtle yet strong effects on the Casimir force. In fact, the Casimir force between a ferromagnetic dielectric and a normal metal might even be repulsive if the role of electron scattering is neglected. In other cases, substantial differences in the force are noted depending on whether, the electron-phonon scattering is included or neglected (Drude model or plasma model) in the calculation of the Casimir force when ferromagnetic plates are used. Thus the measurement of the Casimir force, will also shed light on the role of dissipation mechanisms in the Casimir force.

The specific objectives are the measurement of the Casimir pressure between (1) two ferromagnetic metal plates, (2) a ferromagnetic metal plate and a normal metal, and (3) a ferromagnetic dielectric and a normal metal. A dynamic force measurement technique which directly relates the sphere-plate force to the Casimir pressure between two parallel plates will be used in these measurements.

The experimental group of U. Mohideen (P.I.) at UCR pioneered the use of the Atomic Force Microscope (AFM) a MEMS device for precision measurements of the Casimir force, which has now become a standard technique in the field. They also used it for first demonstration of the lateral Casimir force between two aligned corrugated surfaces and its geometry dependence. They have also demonstrated the role of material properties of the Casimir force with semiconductor materials, and also the optical modulation of the Casimir force. Design of sensors and actuators based on MEMS presently takes into account the role of the Casimir force. Their recent work on the role of carrier density in the Casimir force has already been incorporated into the design of MEMS devices. The technology developed has also been transferred for the rapid and sensitive detection of bio-warfare agents. Given the complexity and interdisciplinary nature of the experiments, there is need for immediate theoretical help. The theorists Professor G.L. Klimchitskaya and Professor V.M. Mostepanenko participating in this work are internationally recognized experts on the Casimir effect (each over 60 papers on the subject). They are an interdisciplinary group with expertise in Condensed Matter Physics and Quantum Field Theory, respectively. A complete understanding of the role of magnetic materials in the Casimir force will be critical for the design of the emerging technology of precision MEMS devices, which are being designed for inertial sensing and communication.

Cold Exciton Gases in Semiconductor Heterostructures

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Funding:	$165,000

An indirect exciton is a bosonic quasi-particle formed by an electron and a hole confined in separated quantum well layers. Due to their properties, indirect excitons form a model system for the studies of basic properties of cold bosons. (1) Indirect excitons have long lifetimes and can cool down to temperatures well below the temperature of quantum degeneracy. This gives an opportunity to realize cold excitons gases. (2) Indirect excitons have built-in dipole moments and their energy can be controlled by voltage. This gives an opportunity to create a variety of potential landscapes for indirect excitons and use them as a tool for studying the physics of excitons. (3) Indirect excitons have long spin relaxation times. This allows studying exciton spin transport and other spin-related phenomena. (4) Indirect excitons can travel over large distances. This gives an opportunity to measure exciton transport by imaging spectroscopy. The objective of our research is to study the physics of cold exciton gases in semiconductor heterostructures.

Electromagnetic Response of Correlated Electron Systems in the Regime of Charge and Spin Inhomogeneity

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Funding:	$135,000

The physics of correlated electron systems is rich and many phenomena discovered in these materials still elude thorough understanding. The complexity of these solids, at least in part, is related to their tendency towards the formation of electronic and/or magnetic inhomogeneities. Evidence for charge/spin self-organization and phase separation in correlated electron materials is overwhelming. 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 study 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 spin/charge ordered states in correlated systems call for the development of novel experimental tools. The proposed program features two new experimental approaches that will allow the PI to significantly advance the present experimental picture of correlated electron phenomena: (1) near-field infrared study of charge dynamics with the spatial resolution down to 10 nm and (2) a spectroscopic investigation of the electrostatic doping in gated structures based on correlated electron solids.

Both of these approaches capitalize on the wealth of information delivered by infrared (IR) or optical probes that have been adapted by the PI specifically to address measurements of correlated electron systems. The capabilities of near-field IR nanoscopy are most valuable when complemented with broad band spectroscopic and/or ellipsometric characterization as recently has been demonstrated by the PI. The electrostatic doping offers an appealing alternative to chemical doping since this method allows one to disentangle intrinsic properties of correlated doped insulators from disorder-driven effects. Tools for IR/optical spectroscopy of gated structures developed by the PI are uniquely suited for the task.

The proposed program will focus on two classes of correlated electron systems: vanadium oxides and graphene. Both classes of materials feature a wealth of new physical phenomena that are yet to be understood. Both classes of materials also hold great promise for technological applications. Therefore the proposed program will allow the PI to explore and exploit novel effects arising in these systems from strong correlations. The nanoscopy studies will be aimed at the systematic investigation of electronic phase separation focusing on the insulator-to-metal transition region in vanadium oxides and low doped or charge neutral graphene. Specifically, near field IR experiments will be performed for various forms of VO_2 and V_2O_3 materials including thin films and single crystals. These nanoscopy measurements will be combined with the nano-scale structural characterization using facilities at the Advanced Photon Source (APS) and with the in-house broad band ellipsometric measurements. The proposed work on vanadium oxides will provide the most complete experimental picture of emergence of the metallic state in this prototypical family of correlated insulators. The graphene component of the program will focus on the methodical studies of the electronic correlations in this new form of two-dimensional electron gas. Broad band IR microscopy carried out by the PI for gated structures will provide insights into systematic variation of many body effects with the level of details previously unattainable for other correlated systems. In-house near-field nanoscopy will augment this with information on the role of electronic inhomogeneities in charge dynamics of graphene.

Nanostructured Materials: From Superlattices to Quantum Dots

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Funding:	$165,000

This proposal is a continuation of a very successful project on “Nanostructured Materials: From Superlattices to Quantum Dots” to be performed at the Nanoscience Group, Physics Department of the University of California, San Diego under the directorship of Prof. Ivan K. Schuller. In addition to in-house research, collaborations which crucially rely on materials and devices developed under this project, are underway at major DOE facilities (synchrotrons and neutron), at UCSD and other research universities. Thus this project is a source of materials and devices used by researchers all across the U.S. and internationally, principally at other DOE funded institutions.

This project is dedicated to the main issues, which arise when materials are nanostructured in one, two and three dimensions. This comprehensive project includes preparation of nanostructures using thin film (Sputtering and MBE) and lithography (electron beam, Focused Ion Beam and self assembly) techniques, characterization using surface analytical, scanning probe microscopy, scattering (X-ray and Neutron) and microscopy techniques and measurement of physical properties (magneto-transport, magnetic and magneto-optical). 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 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.

In addition, this research has potential impact on new applications in important areas of applied research for DOE such as sensors, novel electronics and data storage. Thus development and patenting of important ideas are crucial ingredients in this project. An important and crucial ingredient in this project is the education of the next generation scientists and technologists in state of the art forefront instrumentation, experimental and theoretical techniques. Many young researchers educated in this area have been traditionally employed in industries in the high technology area, have become independent researchers at major research organizations or educators in universities and/or colleges.

Superconductivity and Magnetism in d- and f-Electron Materials

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Funding:	$300,000

During 2011, we have made progress on several fronts, which are summarized below.

Following our earlier discoveries of an anomalous temperature-magnetic field phase diagram in $Yb_2Fe_{12}P_7$, and heavy fermion weak ferromagnetism in $Sm_2Fe_{12}P_7$, we have continued our systematic investigation of non-centrosymmetric “2-12-7” $Zr_2Fe_{12}P_7$-type crystals. We reported on the transport, thermal, and magnetic properties of $Yb_2Co_{12}P_7$, which appears to exhibit short-range correlations well above the temperature where the Yb sublattice orders ferromagnetically. We have also carried out thermopower measurements on several of these compounds, demonstrating that the thermopower is comparable to that found in many strongly correlated systems. In $Hf_2Fe_{12}P_7$, a compound that had not previously been synthesized, we have found that the electrical resistivity has a nearly linear T-dependence at low temperatures, with evidence for a weak antiferromagnetic transition near 5 K. While most of the Co-P based 2-12-7s exhibit ferromagnetic ordering of localized Co moments near 150 K, we recently found that $Nb_2Co_{12}P_7$ appears to present itinerant ferromagnetic ordering near 50 K. We have synthesized a large batch of polycrystalline $U_2Fe_{12}P_7$, which will soon be subjected to neutron diffraction measurements at low temperatures. We have also succeeded in synthesizing some of the corresponding Ni-As based 2-12-7s, and we are now characterizing their properties.

Motivated by our discovery of evidence for cooperative valence fluctuations in $Ce_{1-x}Yb_xCoIn_5$, we have synthesized several single crystalline samples in the series $Ce_{1-x}Yb_xRhIn_5$. We are now in the midst of characterizing these samples to explore whether intermediate valence phenomena exist in this system. Particularly, we are investigating the possibility that the heavy fermion state is also stabilized by cooperative Ce and Yb valence fluctuations.

$PrPt_4Ge_{12}$ was recently discovered and shown to exhibit a high superconducting transition temperature T_c = 7.9 K. The superconducting state breaks time reversal symmetry (TRS). However, the compound $CePt_4Ge_{12}$ exhibits fluctuating valence behavior with no evidence for magnetic order above T ~ 0.48 K. We have synthesized several samples in the pseudoternary system $Pr_{1-x}Ce_xPt_4Ge_{12}$, in order to investigate the possibility that interplay between the superconducting state and Ce-related hybridization effects might produce an interesting phase diagram with new physical phenomena. Thus far, we have established that the substitution of Ce for Pr suppresses the T_c of $PrPt_4Ge_{12}$ monotonically with Ce concentration. We are investigating an anomalous splitting of the feature in the specific heat that is associated with the superconducting transition. We found that the T_c of $PrPt_4Ge_{12}$ is suppressed linearly with pressure.

Electrical resistivity, specific heat, and magnetization measurements on polycrystalline samples of $URu_{2-x}Fe_xSi_2$ reveal a two-fold enhancement of the “hidden order” (HO)/large moment antiferromagnetic (LMAFM) phase boundary $T_0(x)$. The $T_0(P_{ch})$ curve, obtained by converting x to ”chemical pressure” P_{ch} is strikingly similar to the $T_0(P)$ curve, where P is applied pressure for URu_2Si_2 - both exhibit a “kink” at 1.5 GPa and a maximum at ~ 7 GPa. This similarity suggests that the HO-LMAFM transition at 1.5 GPa in URu_2Si_2 occurs at x ˜ 0.2 (P_{ch} ˜ 1.5 GPa) in $URu_{2-x}Fe_xSi_2$. We note that the application of chemical pressure to URu_2Si_2 extends the range of experiments that may be used to study the HO to methods, such as STM, ARPES and PCS that are generally not available in combination with applied pressure, but hold the promise of new insights into the HO.

We have focused a substantial effort on synthesizing several Fe-based superconducting materials in single crystal form. We have successfully synthesized single crystals of KFe_2Se_2. Magnetization measurements on these crystals appear to indicate critical current densities that may be substantially larger than those previously reported for this material. We have also succeeded in synthesizing sizable single crystals of LaFeAsO, and we are now in the midst of synthesizing single crystals of several more members of this family. We have subjected the LaFeAsO single crystals to Hall measurements and have also measured the anisotropy of the electrical resistivity. Previous measurements of polycrystals under pressure resulted in a rather ambiguous phase diagram, due to the broad, difficult to pinpoint feature in the electrical resistivity at the spin density wave transition. The transport signature of the spin density wave is much sharper in our single crystals than in polycrystals, allowing us to more accurately pinpoint the pressure dependence of the spin density wave transition temperature and resulting in a significantly clearer pressure-temperature phase diagram for LaFeAsO. We are also carrying out a study of the effects of actinide substitution on “122” Fe-based superconductors.

Coherent Excitations in Disordered Quantum Materials

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Funding:	$150,000

Disorder-induced structure on the mesoscopic scale can have profound macroscopic consequences, leading to materials with novel electronic, optical, and magnetic properties. This structure can result directly from gross inhomogeneities in a material’s composition or, more subtly, by self-organization on scales from nanometers to microns in the presence of quenched, atomic disorder. The penchant for self-organization is enabled by strong correlations and fluctuations in the near vicinity of a phase transition and can be found, for example, in puddles of electrons that remain on the insulating side of a metal-insulator transition or variegated charge order in high-temperature superconductors. We pick a particularly simple system of randomly-distributed magnetic dipoles to probe the ability of clusters of spins to coherently self organize and decouple from the local environment (“spin bath”). Coherent quantum oscillations of hundreds of spins labeled by frequency in the rare earth tetrafluorides permit the encoding of information and fundamental studies of quantum decoherence mechanisms. We take advantage of the ability to tune quantum tunneling with a “knob” in the laboratory, a magnetic field applied transverse to the ordering axis of the dipoles, and exploit the influence of fluctuations near a quantum critical point, where statics and dynamics are inextricably linked. A combination of multi-axis ac susceptometry, dc magnetotmetry, noise measurements, hole burning, non-linear Fano experiments, and neutron diffraction as functions of temperature, transverse field, frequency, dipole concentration, and excitation amplitude should address issues of stability, overlap, coherence, and random field effects. Extensions to a spin liquid stabilized by geometrical frustration rather than quantum fluctuations, gadolinium gallium garnet, and a quantum antiferromagnet (versus a quantum ferromagnet) promise tests of universality and new models of self-organized collective behavior.

Colloidal Quantum Dot Films. Transport and Magnetotransport

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The project investigates experimentally the electronic transport through self-assembled arrays of quantum dots. The quantum dots are of order 10 nm in diameter or smaller, made by colloidal chemical synthesis. These are materials explored for roll to roll solar cells, cheaper photodetectors and light emission devices. These applications involve and may be limited by the electronic transport through the arrays and 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 is the other aspect of the project. Electrically controlled magnetic material may find use in information storage but such materials are elusive. As the electrons flow only through the lowest level of the dots, which has only spin degeneracy, an external magnetic field can influence the transport through the kinetics of triplet/singlet conversion, the “spin-blockade” effect. Controlling the charge density affects this spin-blockade effect. With magnetic dopants present in the dot, the carriers may produce a magnetic polaron. This may lead to a giant energy shift for the carrier and produce a strong magneto-resistance as well as possible ferromagnetism.

Dynamics of Electronic Interactions in Superconductors and Related Materials

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High energy-resolution angle-resolved photoemission (ARPES) as well as time-resolved laser-ARPES performed with ultrafast lasers will be used to study the dynamics of electron interactions in high temperature superconductors and related materials.

The usual method for accessing the k-resolved electron dynamics (scattering rates) in a solid-state system is through the ARPES linewidth. In the high temperature superconducting cuprates however, the scattering rates obtained by the ARPES linewidths do not match what is observed by other spectroscopies. We correct this with a new method for extracting scattering rates from the superconducting state ARPES spectra, which we also use to more accurately measure superconducting gaps. We perform these measurements as a function of doping level, temperature, and momentum value, giving critical information about the pairing interactions in the cuprates.

By adding the time coordinate to ARPES in ultrafast pump-probe ARPES we also have the ability to separate out non-dynamical effects that serve to broaden the ARPES spectrum, giving a new cleaner window on the electron dynamics.

Transport Studies of Quantum Magnetism: Physics and Methods

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This research program has two main projects: one to study the effect of non-trivial spin texture in itinerant magnets and the other is to develop a shot noise thermometry tailored for the low temperature thermal conductivity measurement.

Recent works in B20 type transition metal compounds have revealed a new topological object in spin systems -- the skyrmion, a particle-like object in which spins point all directions to wrap around the sphere. While neutron scattering and scanning probe experiments by Muhlbauer et al and Yu et al. respectively, confirmed the existence of individual skyrmions and skyrmion lattices in a particular part of the phase diagram, the interaction between skyrmions and electronic degrees of freedom remains to be unveiled. We have been studying the unusual Hall effect in the helical magnet MnSi to find the modification of electron conduction in such a non-uniform spin texture. In particular, under pressure, its Hall voltage displays a distinctive field dependence in addition to the normal Hall effect and the anomalous component arising from the spontaneous magnetization. This additional contribution was observed in a much larger range of temperature and applied field than the so-called A-phase, where the skyrmion lattice was observed in ambient pressure. So far, as the pressure increases, the onset temperature of emergence of this anomaly becomes lower, which suggests that fluctuating, i.e. non-static, skyrmions, instead of forming a lattice, might be present over a broad range of the phase diagram under pressure as the magnetic ordering becomes weakened. We will continue to study the high pressure region above the critical pressure (P> PC ~ 15 kbar), where the magnetic order is supposed to be completely suppressed. It will be expected to shed light on whether the long range order should be required to have such a non uniform spin texture or not and how the transition between two different magnetic happens.

For the shot noise thermometry, we have successfully tested the temperature gradient on stainless steel rod in liquid nitrogen temperature, using two Al-AlOx-Al junctions on separate chips and two calibrated cernox sensors right next to the junctions. Currently we are working on lowering the bath temperature down to 4K to test two junctions on the same chip, which mimics better an actual sample in term of size and distance between the thermometers.

Electric Transport in Novel 2-Dimensional Nanoscale Systems

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The unique electronic band structure of the graphene lattice yields a linear energy dispersion relation, where the Fermi velocity replaces the role of the speed of light. In this relation, the pseudo-spin degree of freedom, originated from the symmetry of wave function in the honeycomb lattice, replaces the role of real spin in the usual relativistic Dirac Fermion spectrum. This additional quantum degree of freedom yields a non-trivial Berry phase, providing the carrier dynamics with a chiral nature. Combined with the real spin degree of freedom, which exhibits SU(2) symmetry, the total internal degrees of freedom of graphene carriers is thus described by a larger SU(4) symmetry, which produces a richer space for potential phenomena of emergent correlated electron phenomena. The major part of this proposal is exploring this unique multicomponent correlated system in the quantum limit.

During the current phase of DOE support, we have laid down the foundation to investigate exotic electron transport behaviors in graphene. We have developed techniques enabling an order-of-magnitude increase in graphene sample mobility, both by suspending graphene above conventional substrates and using a novel hexagonal boron-nitride substrate. With high-mobility samples we have made several significant discoveries and experimental observations: the magnetic field induced symmetry-breaking of the integer quantum Hall effect (IQHE) in bilayer graphene; the discovery of the fractional quantum Hall effect (FQHE) in suspended graphene; and the discovery of a multicomponent FQHE in graphene. We have also demonstrated novel graphene device structures, including Corbino devices, for investigating bulk transport in graphene's magnetically induced insulating state, and mesoscopic thermoelectric devices, for studying thermoelectric and magnetothermoelectric transport phenomena in graphene.

Extending our success from the current period project, we now propose to investigate electron interaction physics in graphene. In particular, we plan to focus our research on fundamental transport properties in high quality graphene samples by probing its correlated electronic states. This effort will be greatly augmented by developing processes to yield high-mobility, homogeneous graphene and hybrid graphene structures to provide material platforms for investigations into possible emergent phenomena. The key scientific issues we are planning on pursuing 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.

Successful completion of this project will lead to new insights into the unique correlated behavior of electrons in graphene. In addition, 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.

Mapping the Electron Response of Nanomaterials

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Funding:	$205,000

Transport or the ability of different materials to conduct energy or electrons remains one of the cornerstones of research in Condensed Matter Physics. What is the nature of an electronic excitation and what determines the lifetime of an excitation remain issues of continuing interest. Research in this area encompasses a range of topics from single particle properties such as electronic structure through to many body properties such as the role of collective excitations including for instance phonons, charge density waves and spin waves. These areas of enquiry acquire a new interest with the emergence of nanoscale technologies. With the ability to engineer new devices at the atomic level the factors that determine communication between these nanoscale entities will clearly influence their practical application. Thus correlation effects are strongly influenced by length scale; and dimensionality and scale determine the many-body excitations available to a system. However issues pertaining to transport in nanoscale systems remain relatively unexplored. Indeed in the last few years, while major advances have been made in the growth of new nanomaterials, the electronic structure of these materials is still relatively unexplored. This program outlined below will have as its scientific focus the use of emerging materials probes, particularly ultrafast and ultrahigh-resolution photoemission and STS (STM), to investigate the change in electronic structure with nanoscale size and dimensionality. Thus the program couples studies of growth with electronic measurements. The program will also develop new scientific techniques for making electronic structure measurements on nanoscale materials and will consist of three major experimental thrusts:

(1) Ultrahigh-energy resolved electronic structure measurements on nanoscale patterned surfaces: Measurements will involve both occupied state and unoccupied state probes, i.e., photoemission and two-photon ARPES. Two major materials systems are envisioned: metallic model systems and metal oxide correlated electron systems.

(2) Study of ultrafast quasiparticle dynamics in low-dimensional nanosystems: Lineshape measurement and ultrafast laser pump-probing will be used to study T1(lifetime) and T2(coherence decay) in nanosystems with the goal being to understand the interrelation of dynamics and dimensionality in artificially fabricated nanosystems. Again, the measurements will use both ultrafast and ultra-high-energy-resolution. ARPES techniques, which will also allow the examination of dynamics processes such as scattering versus parallel momentum.

(3) Investigation of growth and electronic structure: To have an unambiguous investigation of a nanomaterial structure, it is necessary to grow the materials structures in situ in the measurement chamber. As a result, the electronic structure will be examined for various growth conditions. As part of this study, ex situ and in situ STM structure and STS spectroscopy measurements will be used to examine simultaneously the electronic structure of the grown nanobjects. These three experimental thrusts will be matched by a thrust in theory. In particular, this theory effort will focus on investigating the role of the surface in influencing correlated electron effects in surface nanosystems.

Finally, the institutional objective of the program will be to develop a strong collaborative activity between two complementary national groups involved in measurements of electronic structure and dynamics.

Charge Inhomogeneity in Correlated Electron Systems

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Funding:	$99,000

Understanding and exploiting high temperature superconductors is one of the Grand Challanges identified by DOE. In 2008 a new family of high temperature superconductors was discovered based upon iron compounds. There is great excitement that this new class may provide key elements for understanding and mastering high temperature superconductivity. Our group has recently discovered a new material in this family, superconducting films of iron tellurium oxide. We make this new compound by growing films of the non-superconducting parent compound iron telluride, which we can then make superconducting by annealing in oxygen. Alternatively, we can incorporate oxygen during the growth of the film. In either case we make a sample that differs from the parent iron tellurium by the number of electrons in the iron planes, a process known as charge doping. In previous work on bulk materials, iron tellurium was made superconducting by substituting selenium or sulfur for tellurium atoms. Selenium and sulfur have the same electron structure as tellurium, but a different sizes, thus this process changes the spacing of the atoms in the crystal and is known as chemical pressure doping. We have also shown we can synthesize films that combine the two types of doping, for example by oxidizing films of iron selenium. By exploring the effects of this combination of dopants we believe we can better understand exactly how the doping process creates a superconductor from a nonsuperconducting but magnetic parent compound, one of the fundamental unknowns in the field.

These oxidized materials also have properties that look promising for exploring other fundamental questions. The amount charge doping appears to be large enough to alter the basic shape of the Fermi surface, a basic component of the electronic structure. Thus studying this compound can tell us the different types of electronic structure that can support superconductivity. There is evidence that iron tellurium oxide is both magnetic and superconducting, and thus may hold an important place for the study of the detailed relationship between magnetism and superconductivity in the iron compounds.

Fundamental Studies of High-Anisotropy Nanomagnets

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Funding:	$84,000

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.

Simulating Strongly Correlated Electrons with a Strongly Interacting Fermi Gas

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The quantum many-body physics of strongly correlated fermions is studied in a degenerate, strongly interacting atomic Fermi gas, first realized by our group with DOE support in 2002. This system, which exhibits strong spin pairing, is now widely studied and provides an important paradigm for testing predictions based on state-of-the-art many-body theory in fields ranging from nuclear matter to high temperature superfluidity and superconductivity.

Strongly interacting mixtures of spin-up and spin-down 6-Li fermions are produced by using a bias magnetic field to tune near a collisional (Feshbach) resonance. The resonance permits wide tunability of the s-wave scattering length that determines the interaction strength. In addition, the density, temperature, and spin composition are experimentally controllable. Thermodynamic measurements in this system offer unprecedented new opportunities to provide feedback between theory, computation and experiment, which is essential for testing and comparing the best current nonperturbative quantum many-body calculations.

A central feature of our program is the precision measurement of the thermodynamic properties of this unique quantum system, in both the superfluid and normal fluid regime and in three dimensional and two dimensional trapped gases. As the system is strongly interacting, the normal fluid is nontrivial and of great interest, especially in view of a recent conjecture from the string theory community on the concept of nearly perfect normal fluids, which exhibit a minimum ratio of shear viscosity to entropy density.

We made a major breakthrough in our studies of a strongly correlated, resonantly interacting Fermi gas, as described in our recent 2011 Science paper on the first measurement of a transport coefficient, the shear viscosity. At resonance, where the gas exhibits universal behavior, we made the first complete measurement of the universal quantum viscosity. This research combines measurements of the thermodynamic properties (energy, entropy, and temperature) with measurements of the hydrodynamic properties (viscosity).

Measurement of the ratio of the shear viscosity to the entropy density is at present of great interest in the context of a recent conjecture from the string theory community, that the ratio has a universal minimum for a broad class of strongly interacting quantum fields. As both the thermodynamic and hydrodynamic properties can be measured, a strongly interacting Fermi gas offers a nonrelativistic, scale-invariant analog for study. Remarkably, a quark-gluon plasma and our ultracold strongly interacting Fermi gas have nearly the same ratio, about 5 times the lower bound, despite the fact that the temperatures and densities differ by 19 and 25 orders of magnitude, respectively.

Symmetries, Interactions and Correlation Effects in Carbon Nanotubes

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Funding:	$150,000

The project focuses on studying electronic interactions in carbon nanotube quantum dots by low temperature magneto-transport methods. The major research directions include the following:

(1) QUANTUM PHASE TRANSITION IN A RESONANT LEVEL COUPLED TO A DISSIPATIVE ENVIRONMENT

We investigate tunneling through a resonant level formed in a carbon nanotube quantum dot, contacted by resistive metal leads. These leads create a “dissipative environment” for the electrons tunneling across the nanotube, suppressing the tunneling rate at a power law of temperature (with an anomalous exponent equal to the ratio of the lead resistance to the quantum resistance). We developed side-gated nanotube samples, which allow us to control the tunneling barriers between the nanotube quantum dot and the leads. By using the side gates, we can easily tune the tunneling rates from the dot to the two leads to become identical (symmetric coupling) or strongly asymmetric. We study the shape of the resonant peak in the nanotube conductance, while controlling the ratio of the two tunneling rates.

Intuitively, one might expect that both the width and the height of the resonant peak would be suppressed by the dissipative environment, since they both depend on the tunneling rate. However, we find that the result strongly depends on the ratio of the tunneling rate to the two leads. For asymmetric coupling, the peak conductance drops with decreasing temperature, while the peak width saturates. For symmetric coupling, the situation is reversed: the peak width is suppressed at low temperatures, while the peak height saturates at e^2/h. This observation of unitary conductance through a resonance level coupled to dissipative modes is highly non-trivial by itself, and furthermore has implications for a boundary quantum phase transition (QPT) in this system. The dissipation-induced QPTs have been predicted (but never observed!) in more involved quantum impurity models, although surprisingly not for our more basic case. These results have been described in a recent preprint; the PI plans to continue working with the quantum impurity systems in dissipative environment. In particular, we plan to address the Kondo effect in dissipative environment.

(2) KONDO BOX IN CARBON NANOTUBES

The concept of the ``Kondo box'' describes a single spin, antiferromagnetically coupled to a quantum dot that has a finite level spacing. The model has attracted significant theoretical attention, due to an interesting competition between the electronic correlations and confinement. In our recent publication, we have presented the first measurement of the Kondo box, which is formed in a carbon nanotube quantum dot interacting with a nearby localized electron. We have studied the excitations of the Kondo box and characterized the spin of the first few eigenstates. In the regime of partially open tunnel barriers between the quantum dot and the electrical leads, the nanotube conductance has exhibited non-monotonic temperature dependence. We have interpreted this behavior as a two-stage Kondo effect, resulting from competition between two correlated states: the Kondo-box state and the more `conventional' Kondo state coupling the quantum dot and the leads.

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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In the recent past, we have focused on both the synthesis of single crystals of Fe chalcogenides and on the physical characterization of systems synthesized by other groups. We have successfully grown single crystals, by either solid state reaction or the Bridgman technique of Fe_{1+y}Te_{1-x}Se_{x} and performed a very detailed physical and structural characterization of this system. A long manuscript, containing a summary of our efforts is in currently in press at Physical Review B. We have also synthesized K_{1-y}Fe_{2-x}Se_x single crystals, and we are trying to understand the interplay between superconductivity and what seemingly is a Mott insulating state with a well defined gap of ~ 640 K. In particular, we are trying to clarify the role of Fe vacancies, and if the insulating state re-emerges in more underdoped samples once superconductivity is suppressed by an external field, or how this competition affects the superconducting phase boundary at high fields. In high quality LiFeAs single crystals, whose quality is exposed by very narrow Se NMR lines, we have observed a very anomalous irreversibility, both in the magnetic torque and in the magnetization as one approaches the upper critical field. This irreversibility can only be understood if this material has an intrinsic magnetic component associated with the superconducting state, given that it disappears at Hc2. There have been several claims of spin triplet superconductivity in this compound, and we are trying to clarify the behavior of the Knight shift through the superconducting transition. An anomalous Knight shift across the transition in our crystals would further support an unconventional pairing scenario as seen and claimed by other groups. Finally, we have collected a large body of evidence in favor intrinsic vortex pinning in LaFeAsO_{1-x}F_x and SmFeAsO_{1-x}F_x, which is relevant both scientifically and technologically. However, it has been difficult to convince the community that these results are not compromised by impurities and inter-growth in our single crystals, given the low anisotropy of these materials. The large amount of experimental results collected so far, should put us in position to clarify this issue once and for all.

Infrared Optical Study of Graphene in High Magnetic Fields

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Funding: $140,000

In this project, we carry out a systematic magneto-optical study of graphene related materials. Our resent activities were focused on three areas: (1) infrared magneto-spectroscopy of graphite, (2) infrared magneto-conductivity of graphene, and (3) infrared and Raman spectroscopy of topological insulators.

(1) In this work, the electronic structure of graphite was investigated by high field magneto-infrared reflectance spectroscopy. High fields lift the degeneracy of the intriguing electron-hole mixed Landay levels and resolve the electron-hole asymmetry of the interband transitions. Both Schrödinger-like (K-point) and Dirac-like (H-point) Landau level transitions are observed. In order to quantitatively analyze the Landau level transitions at high fields, we derived a new analytical formula in a limiting case of the Slonczewski-Weiss-McClure model to account for both of the nonlinear magnetic field dependence observed at high fields and the electron-hole asymmetry, and extracted band parameters.

(2) Our first IR magneto-photoconductivity measurements on single-layer graphene on BN show great ability for identifying quantum Hall states. Measuring the photoconductance also reveals a dependence on Landau level (LL) filling factor, with changes in the conductivity as LLs are entered and exited. While the resolution of the photoconductance measurement is weaker than transport measurements, the photoconductance will be used to probe bulk excitations caused by circularly polarized light. The experimental setup for mid-IR circular-polarized photoconductance was developed.

(3) Inelastic light scattering was used to probe low-energy excitations in Bi_2Se_3 and Sb_2Te_3 single crystals. We accurately studied the temperature dependence of of dominant Raman-active phonons over the temperature range from 5 K to 300 K. The temperature dependence of the Raman peak position and linewidth is analyzed considering the anharmonic decay of optical phonons and the material thermal expansion. This work suggests that Raman spectroscopy can be used for thermometry in Bi_2Se_3- and Sb_2Te_3-based devices in a wide temperature range.

Microwave and rf Spectroscopy of 2D Electron Solids and Stripes

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Funding: $102,000

The project is on experimental studies of high magnetic field, electron solid states in two-dimensional electron systems and bilayers. Such states occur in sufficiently low-disorder systems when magnetic field freezing out the kinetic energy degree of freedom A 2D electron system (2DES) in a low Landau filling pinned Wigner solid state exhibits a striking resonance in its rf or microwave spectrum. The resonance is the focus of our research, and is understood as a pinning mode, in which the electrons oscillate about their pinned positions, and the frequency, fpk increases for larger disorder.

During the fiscal year we (1) submitted a paper to Phys Rev B on bilayer samples with unequal densities in each layer; (2) continued studies of Wigner solids within fractional quantum Hall effects; (3) put together results on an extensive study of electron solids in wide quantum wells, for submission shortly; and (4) began work on samples with the 2DES resident in dilute AlxGa1-xAs, with obtaining data to 14 T on samples with x=0.4 and 0.8 %.

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

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This project prepares high quality single and polycrystalline samples of iron pnictide (FePn) and related superconductors, as well as novel f-electron quantum critical systems. These samples are 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 30 T routinely, and 45 T upon need. 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. Measuring the specific heat of the FePn superconductors as a function of magnetic field, as well as a function of angle in field, provides valuable information in determining the nodal structure of the superconducting gap. Further objectives include investigating the relation between magnetism/magnetic fluctuations and the superconductivity in the new FePn superconductors, with a focus on whether the superconductivity is unconventional.

Novel States of Matter in Filled Skutterudites and Related Materials

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Filled skutterudites is a large class of technologically important materials that display properties and behaviors, challenging our understanding of matter. An essential ingredient of this crystal structure is the presence of large voids that can accept rare earth atoms. Weak binding of the filler atoms is the source of characteristic lattice dynamics, rattling, which affects electronic properties and leads to physical phenomena not found in other physical systems. This weak binding makes filled skutterudites the most promising materials for future thermoelectric applications.

The crystal structure being remarkably insensitive to the size of the filler atom provides an unparallel opportunity to investigate relationships between various states and behaviors. By partial replacement of one filler atom by another we investigate relationships between poorly understood ground states of matter and coexistence of states considered to be incompatible with each other in a single crystal structure.

Of particular interest are unconventional superconductivity, hybridization gaps and pseudo-gaps, and novel heavy fermion behavior in Pr-based systems. The emphasis is on establishing the nature of multiple superconducting phases and transitions in $PrOs_4Sb_{12}$ and establishing the mechanism of unconventional superconductivity. The project explores the role of phonons in strongly correlated electron systems by investigating correlations between electronic properties and rattling characteristics in hybridization gap materials.

New materials are designed and synthesized using either single-crystal flux growth method or arc-melting. Measurements are performed in a wide range of temperatures, down to 20 mK, and in the highest magnetic fields currently accessible.

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

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Funding:	$165,000

This project studies a variety of solids using infrared synchrotron radiation. A major emphasis is non-equilibrium effects using pump-probe spectroscopy. These experiments employ short laser pulses in the near infrared or visible to make photoexcitations; the probe light is ~200 ps synchrotron radiation and can be varied over a very wide wavelength range, from the far infrared through the visible, as appropriate for the physics under study. We also do linear spectroscopy, exploiting the high brightness of the far-infrared synchrotron radiation when high performance is needed. We have studied the linear and the photoinduced absorption in type-II superconductors as a function of temperature and magnetic field strength. Field orientation matters in these experiments. For fields parallel to the film surface, the field alters the orbital motion of the quasiparticles, breaking the time-reversal symmetry of the condensate pairing and reducing the gap, as originally proposed by Abrikosov and Gor'kov and observed here for the first time. For perpendicular field, vortices dominate the far-infrared response. In photoinduced absorption studies, we measure the photon-energy-integrated change in far-infrared transmission as a function of time after Cooper pars are broken by photoexcitation. There is a bottleneck in the recombination process, because a gap-energy phonon is emitted and this phonon has a high probability of breaking another Cooper pair. We have studied and characterized this bottleneck. We observe that a magnetic field significantly slows recombination and attribute the slowing to the gap change induced by the field. We have also studied a variety of other materials, including the supermetallic properties of Br-doped graphite, lattice effects in multiferroics and high dielectric constant insulators, fast processes in compound semiconductors, use of silica aerogel as a broadband tunable waveplate, and terahertz emission from silicon CMOS oscillators.

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

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Subjecting materials to conditions far from equilibrium leads to otherwise-unattainable properties. For example, the steady state photoexcitation of a high mobility quasi-two dimensional electronic system based on the GaAs/AlGaAs semiconductor induces periodic-in-the-inverse-magnetic-field, large-amplitude Radiation-induced Magneto-resistance Oscillations (RIMRO), with novel Radiation-induced Zero-resistance States (RIZRS) characterized by activated transport without concomitant quantum Hall effect. This project aims to experimentally extract new insight into the origin of these radiation-induced zero-resistance states and associated magneto-resistance oscillations, which constitute a new example of emergent behavior in a driven, steady-state, non-equilibrium system.

Over the past year, we designed and fabricated a novel setup including a circular waveguide where the polarization could be rotated continuously over 360 degrees with respect to the long-axis of the Hall bar situated within the cryostat at liquid helium temperatures. Experiments using this setup, which are still being refined, are now being carried out, and they are yielding exciting and surprising results. For example, we have found a strong and unexpected sensitivity of the radiation-induced transport phenomena to the angle between the current in the device and the microwave electric field. We hope to continue using the polarization as a new parameter in investigating the photo-excited transport. We are also examining microwave reflection and transmission from the 2DES with the aim of establishing further correlations with the transport response.

An effort is also being developed in the area of photo-excited transport in graphene. Here, the effort is carried out in collaboration with the Georgia Tech group, which did pioneering work in the field. Finally, we are also examining transport in the topological insulator Bi_2Te_3.

At present, this group consists of the PI, a postdoc, 6 graduate students, and 5 undergraduate students.

Spin Polarized Electron Transport Through Aluminum Nanoparticles

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Funding:	$130,000

We have developed a technique to study magnetic properties of individual ferromagnetic nanoparticles of diameters down to 2nm. Measuring such extremely small ferromagnets is very difficult, and there have been very few successful measurements in this regime before this work. Our technique combines electron tunneling spectroscopy and microwave pumping. The tunneling current through the nanoparticle versus magnetic field displays magnetic hysteresis, while the tunneling leads are used as coaxial lines to apply microwave fields and pulses on the nanoparticle. Using this technique, we studied for the first time the time scale for the relaxation of the magnetization in single Co nanoparticles. The magnetization relaxation time is ~microsecond, indicating reduced damping in ferromagnets with strongly reduced dimensions.

We have also found that the magnetic hysteresis loop is very sensitive with respect to the bias conditions (voltage or current). The magnetic switching field at mK-temperature is strongly reduced as a function of bias voltage: at 10mV bias voltage, the switching field is reduced by 15%, while the magnetization can be switched by applying a voltage pulse of 10mV. We speculate that the strong reduction of the switching field with voltage represents the case of magnetic excitation driven by the tunnel current, and the strength of the effect displays enhanced coupling between magnetic excitation and the tunnel current in ferromagnets with strongly reduced dimensions. The enhancement of the coupling between magnetization and the bias conditions suggests a regime very different compared to that in larger ferromagnetic samples. That is to say, extremely small ferromagnets are much more excitable by biasing that in the bulk. Future work will try to understand the enhanced sensitivity of the magnetization to the bias conditions.

Electron Imaging in Graphene

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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 develop new devices. Westervelt's group is using a liquid He cooled scanning probe microscope, to image electron motion through graphene devices. The conducting tip acts as a movable gate that changes the electron density immediately below and scatters electron waves. Devices fabricated from suspended graphene sheets promise to increase the electron and hole mean free paths into the ballistic regime. These devices are shaped using the electron beam of Harvard's high-resolution transmission electron and scanning transmission microscopes.

Quantum Materials at the Nanoscale

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Funding: $1,700,000

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. Some highlights of our work during FY2011:

Highlight 1. Measuring fractional vortices in Sr_2RuO_4 (SRO): Following a suggestion by Leggett, Budakian fabricated micron-sized, ring-shape structures from high-quality samples of SRO (from Y. Maeno, Kyoto U.) using the focused ion-beam capabilities at the MRL Central Facilities. Budakian's group made ultra-sensitive cantilever magnetometry measurements on these SRO rings and discovered vortex states exhibiting a magnetic response consistent with the presence of half-quantum vortices, in results that were recently published in Science and featured in a Search and Discovery article in Physics Today.

Highlight 2. Fundamental studies of electronic correlations and phase coherence using graphene: Hughes, Goldbart, and Mason determined the spectra of individual Andreev Bound States (ABS) that formed in a graphene quantum dot; the results are reported in a recent Nature Physics paper. Mason fabricated narrow superconducting tunnel probes, as well as normal-metal end contacts, on top of exfoliated graphene flakes, leading to the creation of potential wells, or quantum dots, that were proximity coupled to the superconducting probes. The interplay of the resulting Andreev reflections with Coulomb charging effects gave rise to low-energy ABS seen in tunneling measurements.

Highlight 3. Magnetostructural phases and mesoscale domains in magnetically frustrated Mn_3O_4: To study magnetic frustration and associated effects in strongly spin-lattice coupled materials, Cooper grew large single crystals of frustrated Mn_3O_4, which were measured by Abbamonte (X-ray) and Cooper (Raman). These results showed that magneto-dielectric behavior in Mn_3O_4 is associated with field-induced tetragonal-to-orthorhombic distortions. More recent magnetic field-dependent Raman and X-ray diffraction measurements at the X21 beamline at Brookhaven NL confirmed that there is a field-tuned quantum (T ~ 0) phase transition to a frustrated tetragonal spin/orbital glass phase in Mn_3O_4.

Highlight 4. Anomalous Noise in the Pseudogap Regime of $YBa_2Cu_3O_{7-d}$: Van Harlingen and Fradkin observed an unusual noise component near and below about 250 K in the normal state of underdoped YBCO and Ca-YBCO films. This noise regime, unlike the more typical noise above 250 K, has features expected of a symmetry-breaking collective electronic state (e.g., charge nematic order), including large individual fluctuators, magnetic sensitivity, and aging effects.

Highlight 5. Measurement of the effective fine structure constant of graphene: To investigate how screening influences the strength of interactions in graphene, Abbamonte performed inelastic x-ray scattering experiments on single crystal graphite at Sector 9 at the Advanced Photon Source. Using new reconstruction algorithms developed in collaboration with Fradkin, Abbamonte imaged the dynamical screening of charge in a freestanding graphene sheet, finding that the strength of Coulomb interactions is characterized by a scale-dependent, effective fine-structure constant, which approaches the value 0.14 ~ 1/7 at low energies and large distances. This value is substantially smaller than past estimates and suggests that graphene is more weakly interacting than previously believed. This study—which recently appeared in Science —is significant because it demonstrates that a two-dimensional system can exhibit strong dielectric screening over finite distances, provided its excitation spectrum is gapless.

Investigation of the Stability and Dynamics of Nanoscale Magnetism Using Superconducting Probes

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Funding:	$120,000

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-x} (A=Ca,Sr,Ba; B=Mn,Fe,Ru) and R-type ferrites $(Ba,Sr)M_{2+x}Ru_{4-x}O11$ (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 addresses the following questions:

(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.

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.

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 $0 < m\mu_{zero} H < 14$ 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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Funding: $170,000

We are currently working on two separate but related projects. The first is a magnetotransport study of the effects of the exchange field in Be/EuS bilayers, where EuS is a ferromagnetic insulator. Specifically, we are using the proximity induced exchange field in ultra-thin Be films to produce large low-field magnetoresistances. We fabricate the samples so that the Be component of the bilayers has a zero field sheet resistance well above the quantum resistance. In this regime the Be exhibits a multi-fold negative magnetoresistance over a field of a couple of kG. We believe that the application of a relatively small external field greatly enhances the exchange field in the films, thereby causing the anomalously large magnetoresistance.

The second project follows up on our recent study of electron glass behavior in ultra-thin Be films. In these experiments we are investigating the effects of a large Zeeman field on the observed non-equilibrium dynamics of the films. Our goal is gain a better understanding of the electron glass phase by tuning the Zeeman splitting in a high parallel magnetic field.

Infrared Hall Effect in Correlated Electronic Materials

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This project addresses the physics of correlated electronic materials using spectroscopic measurements of the magneto-optical response at infrared frequencies. The materials under investigation are the hole-doped cuprate superconductors, and topological insulators. These novel materials offer important potential applications in miniaturization of electronics, multifunctional sensor and data storage applications, energy storage, spintronics, and quantum information technology. The project confronts important open questions in the optical and transport properties and the electronic structure of these correlated metals by using infrared magneto-optical experimental results together with ongoing collaborations with theorists and the results from other experimental probes. Measurements are made in magnetic fields to 8 T and temperatures from 1.2 K to room temperature. Polarization modulation techniques allow sensitive measurements of the Faraday and Kerr rotation and circular dichroism, which allow the determination of the full magneto-conductivity tensor. This provides the frequency dependence of the diagonal and off-diagonal conductivity, the Hall angle and the Hall coefficient.

In the first year of the project the main effort was on Bi_2Se_3, an example of a topological insulator which is a new quantum state of matter predicted by theory. THz magneto-optical measurements were made to characterize the material and to investigate the topologically protected non-degenerate chiral surface state predicted by theory. Gated Kerr rotation measurements revealed the THz magneto-transport properties of the surface states. Methods to improve the surface quality and THz response were developed. This preliminary work laid the groundwork toward THz applications of these materials and pointed the way toward enhancing the surface state properties through improved materials and surface passivation.

The current and future effort of the project will be on the cuprate superconductors. The main goal of this work is to account for the transport properties of the cuprates in terms of the Fermi surface information available from ARPES and the other experimental probes. Our IR magneto-optical data is being critically compared with the data from Angular Resolved Photoemission Spectroscopy (ARPES), transport measurements (especially quantum oscillations), conventional optics, Scanning Tunneling Microscopy (STM), Raman studies and other experimental probes of these materials. The focus of the effort is on the underdoped cuprates where quantum oscillations have been observed in transport measurements.

Measurement of Single Electronic Charging of Semiconductor Nano-Crystal

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Funding: $150,000

Efficient conversion of solar into electrical energy requires materials that capture a large fraction of the photons from the sun, use these photons to create electrons and holes, and allow the electrons to come out of the material with high probability. Semiconductor nanocrystals (NCs) are attractive materials for this application because the photon energies they absorb can be tuned by changing their size, and because the absorption of photons by NCs is known to cause excitation of electrons in them. The major challenge is to remove the charge carriers efficiently. The objective of this project is to measure the motion of electrons in arrays of semiconductor NCs in order to determine what limits the charge collection. We propose to build devices that can measure the electrical charge distribution in two-dimensional arrays of NCs. We will make devices with response times short enough to study how the charge distribution changes with time. The trapping of charge is thought to interfere with extraction of electrical energy from NCs, so it is important to find out how much charge is trapped and how long it remains trapped. We have developed techniques, using nanometer-size Si Metal Oxide Field Effect Transistors (MOSFETs) for the measurement of charge and how it changes in thin films of semiconductors, such as amorphous Si, another solar material. However, these techniques have not been applied to NCs. We have developed techniques for patterning the NC arrays on the nanometer length scale and are now preparing to measure the charge on the arrays and its time dependence as a function of applied voltage and under exposure to light. We will use a variety of NC materials, prepared by out collaborators, who are chemists. By varying the semiconductor and the NC diameter one can tune the absorption of photons over a wide range, covering the entire solar spectrum.

Novel Temperature Limited Tunneling Spectroscopy of Quantum Hall Systems

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Funding:	$150,000

Spectroscopic methods involving injection or ejection of electrons in materials have unique power in probing the electronic structure and interactions between electrons. The “single particle” spectrum obtained from techniques such as photoemission or tunneling spectroscopy is among the most fundamental and directly calculable quantities in theories of highly interacting systems. In ordinary superconductors, comparison of features in this spectrum with theory proved to be one of the primary experimental signatures validating the BCS theory of superconductivity. We are developing a fundamentally new spectroscopic technique, time domain capacitance spectroscopy (TDCS), to measure the single-particle spectrum of the 2DES in semiconductors and of graphene without a perturbing scanning tip and with negligible electron heating, even when the in-plane conductivity of the system vanishes. The TDCS results have yielded unprecedented high-resolution measurements of the cold 2DES over a range of 20 meV (~200 Kelvin) above and below the Fermi surface. These measurements reveal the difficult-to-reach, beautiful, and surprising structure in this highly correlated system far from the Fermi surface. Our planned work extends the use of the TDCS technique to the 2DES at lower temperatures and with higher energy resolution, to edge states of the 2DES, and to the 2D hole system. The TDCS technique will be used to search for and characterize, with extraordinary resolution, features in the single-particle spectrum of semiconductors at energies both close to and well away from the Fermi energy. TDCS has already revealed a number of surprises in the quantum Hall system, and the work to be performed may reveal signatures of new quasiparticles, the nature of quantum Hall edge states, and the properties of the low carrier density 2D system as the carriers order to form an electronic crystal. With this progress, TDCS can grow to be applied to technologically important systems such as high-Tc superconductors, graphene, topological insulators, and spintronics systems to provide fundamental and previously unattainable data on the electronic properties of these materials.

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

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Nanocrystals (NCs) of semiconductors have been incorporated into hybrid organic/inorganic solar photovoltaic devices for increased light absorption, increased charge separation rate, and enhanced mobilities. NCs of semiconductors of the II-VI family such as CdSe or CdTe and of the IV-VI family such as PbS and PbSe have recently been the subject of increasing study and controversy for their potential in improved 3rd generation solar cells through the generation of more than one electron-hole pair per photon (the carrier multiplication controversy). Morphologies ranging from spherical quantum dots, high aspect ratio quantum nanorods, and branched morphologies such as tetrapods have been studied as potential materials for an optimized hybrid solar cell. Hybrid nanostructures or organic/nanocrystal structures that aim to break up excitons and funnel charge within a device are actively being pursued. The foundation of all this activity is the synthesis and thorough characterization, both structural and optical, of the NCs themselves.

Given the potential impact of devices that use NCs as a functional material in the energy field, it is crucial to understand at a very basic level the optical physics, both static and dynamic, of NCs of a variety of materials and morphologies. Without such understanding, designing novel structures, novel device architectures, and understanding the potential and limitations of present materials and devices is haphazard at best. A basic understanding of the optical physics of semiconductor NCs is the core aim of this proposal. 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 proposal 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, (4) probing the potential for coherent electronic coupling between J-aggregates and NCs using 2-D Electron Spectroscopy, (5) probing the dynamic quantum confined Stark effect in NCs at the single NC level and (6) measuring the absorption spectrum of a single large nanocrystal or nanocrystal heterostructure optimized for incorporation into a NC hybrid solar cell.

Quantum Transport in Topological Insulator Nanoelectronic Devices

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This proposal describes a research program designed to play a leading role in the field of nanoscale quantum electronic transport. The research addresses a current central theme in condensed matter physics: the conceptually new behavior of electrons in solids whose effective Hamiltonian is described by the Dirac equation and whose electronic properties are protected by fundamental symmetries of the materials band structure. In particular, the research objective of this proposal is to investigate novel quantum transport phenomena in topological insulators.

Topological insulators (TIs) are materials with a bulk band gap but which have a conducting surface state. This surface state has two special properties: (1) it exhibits a relativistic-like linear energy-momentum dispersion, analogous to grapheme, and (2) its conducting character is protected by time reversal symmetry. The latter confers the surface state its topological protection, i.e., the surface state remains gapless even in the presence of moderate disorder. The unique geometry, band structure and topological characteristics of the TIs have generated an extraordinary interest in the physics community and have led, together with graphene, to the emergence of a new paradigm of "relativistic" condensed matter physics. This research proposes to measure fundamental quantum phenomena, such as superconductivity, the quantum Hall effect and excitonic condensation in new regimes made possible by the TI's two-dimensional surface state geometry, topological characteristics and relativistic-like band structure. A crucial element of the proposal is the fabrication and characterization of high quality thin TI devices, by using both exfoliation from single crystals and by growing TIs epitaxially by MBE. Electronic transport measurements as a function of temperature and magnetic field will reveal insights into a wealth of phenomena predicted by theory, including weak antilocalization, exotic types of quantum Hall effect, Klein tunneling, and excitonic superfluidity.

Particular efforts will be devoted to the study of quantum states which occur at the interface of TIs with superconductors, where excitations with unusual quantum statistics (different from bosons or fermions) called Majorana particles can be realized. The vision of electronics based on such particles is of profound importance for both scientific research and technological applications, and is considered among the holy grails of present condensed matter research. Specifically, non-Abelian particles allow the generation and manipulation of dephasing-tolerant quantum states which are crucial for quantum information, and promising for addressing long-standing questions in quantum physics.

To seek for non-Abelian particles, we will measure tunneling into a superconductor-TI interface, and study the supercurrent flowing through superconductor-TI-superconductor Josephson junctions. Furthermore, advanced geometries which allow the localization and manipulation of those elusive particles will also be studied. We will also probe the limits of the TI state by building ultra-thin samples, where 3D to 2D dimensionality transitions and condensation effects are expected.

The Jarillo-Herrero group is well positioned to tackle this research project, with strong experience in device nanofabrication, low temperature precision transport measurements, and a proven record of studying quantum transport phenomena in low dimensional carbon materials. Such experience will prove invaluable when studying quantum Hall and the advanced superconductor-TI devices proposed here. In addition, the PI is already investigating high quality TI single crystals and thin films grown by MBE, and he has recently published one of the first reports of surface state transport and electric field effect on TI nanodevices.

TI research spans into many areas of physics, from high-energy physics, where many of the topological concepts applicable to TIs have been developed, to research on thermoelectric materials and energy harvesting, since most of the TI materials are based on Bi compounds known for their thermoelectric properties. The PI will stimulate a strong interaction between education and research which will result in excellent training for postdoctoral fellows, graduate and undergraduate students, who will acquire the necessary skills to become accomplished experimental condensed matter scientists. Recruiting efforts by the PI will contribute to the integration of women, minorities and international students, especially from developing countries, into the scientific community.

Nanoscale Magnetodynamics and Beyond

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Funding: $82,000

Recently, in collaboration with Hitachi Global Storage Technologies (HGST), we reported novel magnetostatic and magnetodynamic effects in coupled nano-dot chain arrays. Permalloy (PY) dots 300 nm in diameter and 40 nm thick were formed, via e-beam lithography, into a square lattice with 350 nm lattice constant. Samples were prepared with five dot chains coupled by PY bridge widths of 0, 20, 40, and 60 nm. Bridge exchange coupling significantly suppresses vortex formation and the ensuing buildup of exchange energy is release by simultaneous reversal of the magnetization and vortex nucleation. The magnetodynamics were investigated with the magnetization saturated normal to the film plane. The no-bridge spectrum is consistent with ‘drum-head’ type Bessel function modes. Coupled dots produce increasingly complex mode structures with increasing coupling strength. Simulations demonstrated that the additional satellite structure on the higher order (lower field) modes arise from a single dot-bridge component within the chain—the structure increasing in complexity as the bridge becomes a larger part of this component. Simulations also demonstrated that normal mode excitations arising from interdot coupling appear as satellites on the immediate low field side of the lowest order (highest field) resonance, which increase in intensity and separation with increasing coupling strength. As an extension of this project, we are doing simulations of magnetodynamics of exchange coupled magnetic nano-wires. Based upon the simulation results, HGST will fabricate, via e-beam lithography, the samples optimized for inter wire transfer of spin waves.

In collaboration with Dan Dahlberg at the University of Minnesota and Caroline Ross and Carl Thompson at MIT, we began an investigation of magnetostatics and magnetodynamics in single crystal Ni films grown on MgO at MIT. To date we've measured the ferromagnetic response as a function of in-plane angle and temperature at 36 GHz. Next we will measure at 10 GHz allowing us to extract intrinsic versus extrinsic contributions to the magnetic damping. The goal if this investigation is to compare resonance damping (MU) with electron transport (UMN).

In collaboration with Chris Leighton at the University of Minnesota, we are investigating CoS_2, a promising model system for fundamental studies of spintronic processes. This system has - 55% spin polarization (P) at the Fermi level, a value that is tunable with Fe doping in $Co_{1-x}FexS_2$, reaching + 85%. Of interest is whether the ferromagnetic damping is influenced by P. Single crystals of in $Co_{1-}xFexS_2$ with close to ideal sulfur stoichiometry are ground into powder for the FMR studies. The linewidth exhibits a minimum at T_C, which provides a measure of both T_C and the breadth of the FM transition. In contrast to expectations based on NMR, the linewidth is observed to increase rather than decrease with increasing P. This suggests that other mechanisms, such as two-magnon scattering or Fe positional inhomogeneity, dominate the damping. We observe also the absence of a paramagnetic resonance well above T_C, indicating the absence of a localized moment above the ordering temperature.

Novel Behavior of Ferromagnet/Superconductor Hybrid Systems

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Funding:	$168,000

When ferromagnetic (F) and superconducting (S) materials are put in contact with each other, new properties emerge, which differ from the properties of either of the components. In addition to their intrinsic scientific interest, such hybrid S/F systems may have applications in new types of superconducting electronics or in quantum computing. The primary scientific objective of this project started out as a search for a new kind of superconducting pair correlations predicted to occur in S/F systems in the presence of certain forms of magnetic inhomogeneity. The new type of superconductivity involves electron pairs with parallel spins (spin-triplet pairs), rather than the usual anti-parallel spins (spin-singlet pairs), even though the conventional superconductors by themselves generate only spin-singlet pairs. Our search was based on measurements of S/F/S Josephson junctions where the spin-triplet pairs have a clear signature; spin-triplet pairs produce a supercurrent that extends over a long distance in F, in contrast to the very short distance scale characterizing spin-singlet supercurrent. In the fall of 2009, our search was successful. By combining three distinct magnetic layers in our samples, we were able to generate a long-range supercurrent in samples containing a thick central layer of cobalt, which is a strong ferromagnetic material. Our first paper reporting these exciting results was published in April of 2010; it has been well-received in the field and has already garnered 43 citations. The focus of our work has now shifted toward three new goals: (1) optimizing the generation of spin-triplet pairs by better controlling the magnetic state of the sample, (2) exploring other ways to detect spin-triplet pairs besides measurements of Josephson junctions, and (3) learning how to control the spin-triplet supercurrent (i.e., turn it on and off) in a single sample. We have made progress toward the first two of those goals, and are continuing to work on all three.

As always, our work has educational goals as well as the obvious goal of impact on the field of condensed matter physics. Two graduate students have already received their Ph.D.'s based on work on this project. Three graduate students are currently working on the project, one of whom is expected to graduate in 2012. In addition, several undergraduate students have contributed to the project, and are now enrolled in prestigious graduate programs around the country.

Mechanisms for Surface Segregation in Compound Semiconductor Thin Films

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Funding:	$35,000

The goal of this program is to determine the atomistic mechanisms for surface segregation in III-V semiconductor alloy systems. Central to this is to understand the atomic surface structure of alloy surfaces. We use both experimental and computational approaches to achieve these goals. We determined which factors affect the complex structure seen in InGaAs strained layers. Specifically, we showed that surface ordering is governed by both energetic and entropic effects, and that the coverage of the different reconstructions depends on growth conditions. Furthermore, we elucidated the incorporation of Sb into the GaAs substrate, and examined the effect of the surface reconstruction on the stability of dislocations. We have studied the incorporation of Bi on GaAs and calculated a full phase diagram for the possible structures as a function of growth conditions.

Emergent Phenomena in Quantum Hall Systems Far From Equilibrium

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Funding:	$130,000

The main objective of the research project supported by this grant is to study the emergent behaviors of high mobility two-dimensional electron gases formed in semiconductor heterostructures which are driven out of equilibrium by dc and/or microwave electric fields. Recent developments in the area of non-equilibrium transport in low magnetic fields revealed many new fascinating phenomena. Among these are 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. All of these remarkable effects are usually observed at temperatures above 1 Kelvin in the regime of very high Landau levels when Shubnikov-de Haas oscillations are strongly suppressed by disorder and/or temperature. In contrast to the majority of past research efforts, this project will study the experimental regimes of lower Landau levels and lower temperatures, which remain essentially unexplored. One of the outstanding questions addressed by this project is the nature of recently discovered dc-induced states with zero differential resistivity observed in the Shubnikov-de Haas regime and their possible relation to phenomenologically similar states observed in very high Landau levels. Another issue of interest concerns the implementation of the non-linear resistivity as a probe for the electronic density of states. In addition, the project will study the effects of dc and/or microwave electric fields on the Shubnikov – de Haas oscillations which remain very poorly understood. Finally, the project will explore the possibility of extension of the any of the microwave-induced or dc-induced effects established for electrons in very high Landau levels to the quantum Hall effect regime to study composite fermion states. The work on this project will allow us to better understand how these emergent effects originate from the behavior of individual electrons due to the complexity of their competing interactions with other electrons, electromagnetic fields, static disorder, and lattice vibrations.

Tunneling and Transport in Nanowires

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Funding:	$140,000

The goal of this program is to obtain a fundamental understanding of phenomena that might be relevant to the performance of devices and circuits at the limit of the smallest realizable feature sizes. The approach is to study structures prepared using physical rather than chemical or biological techniques. The main focus of the work will be on the investigation of selected properties of nanowires that are either quasi-one-dimensional (quasi-1D) or one-dimensional (1D). Which term is appropriate depends upon the size of the widths and thicknesses, or radii, characterizing the transverse dimensions of the wire relative to some characteristic length associated with a physical property that might be altered by dimensional constraint. When these lengths are smaller than the inelastic scattering, phase coherence, or superconducting coherence lengths, the wires are quasi-1D. This distinguishes them from wires for which the transverse dimensions are smaller than the Fermi wavelength where 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. In 1D even weak interactions destroy the conventional Fermi surface. It is important to further probe this regime and to understand the entry into the TLL regime produced by either reducing wire size or by changing the wire carrier concentration.

We are carrying out two types of experiments on nanowires prepared using electron beam lithography (EBL). The first type involves selected experiments on 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. Such devices may exhibit longer coherence times than those based on oxide barrier junctions. We are attempting 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 are searching for h/e flux quantization in nanometer scale superconducting loops, which may reveal the nature of Cooper pairing in mesoscopic systems. Finally we are studying the superconductor-insulator transition in nanowires, by varying their thicknesses, their coupling to dissipation, and their charge densities. The latter will be accomplished using electronic double layer transistor configurations. We have developed a technology of electrostatically doping materials using ionic liquids in an electronic double layer transistor configuration.

The second type of experiment will be directed at exploring the TLL regime of a new type of 1D wire, prepared from a low carrier density material, either electrostatically doped $SrTiO_3$ or $KTaO_3$. We would employ electron beam lithography to form a surface mask, and would then use an ionic liquid to induce charge in an exposed line 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. We would then study charge and spin transport in detail, and by employing electrostatic gating, tune between the 1D and quasi-1D regimes so as to determine the phase diagram as a function of carrier concentration.

Studies of Artificially Structrured Composite Magnets

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Funding: $115,000

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.

Thermal Conductivity and Thermopower Near the 2D Metal-Insulator Transition

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Funding: $150,000

The availability within the past decade of two-dimensional electron systems in samples of very high mobility has enabled the study of new and very interesting physics in strongly interacting electron systems, a region that had previously been inaccessible. The discovery in this regime of a totally unexpected transition to metallic behavior, which is forbidden in weakly interacting systems, has elicited enormous experimental and theoretical interest and activity. Most of the experimental investigations have focused on the transport behavior - the longitudinal and transverse resistivities with and without magnetic field. Quite surprisingly, there have been few studies of the thermal properties, either theoretical or experimental. The aim of the present proposal is to study the thermoelectric power and the thermal conductivity of dilute two-dimensional electrons systems in high-mobility samples near the 2D MIT in the ballistic and diffusive regimes, and to determine the effect of in-plane magnetic field on the thermal response. It will be particularly interesting to compare the results with the earlier results on the resistivity. Experiments are being done in Sarachik's lab at City College and Kravchenko's laboratory at Northeastern University. It is anticipated that these studies will yield important results in relatively uncharted territory.

Quantum Coherence and its Manipulation in Coupled Quantum Dots

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Funding:	$148,000

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 carriers.

Antiferromagnetism and Superconductivity

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Funding:	$150,000

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 that is so important in applications of superconductivity in magnetic fields. We are studying the doping sensitivity of magnetism in the vortex cores in $Bi_2Sr_2CaCu_2O_{8+d}$, carried to very high magnetic fields. Secondly, we are investigating the vortex dynamics in the new class of pnictide superconductors using a sensitive, microscopically-based tool, NMR spin-spin 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. 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.

Experimental Study of Severely Underdoped Ultrathin Cuprate Films

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Funding:	$85,000

This project has generally proceeded along 4 parallel lines. The most important is our study of the superfluid density of “thick” films of $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi-2212), grown by one technique (pulsed laser deposition) at OSU and another technique (sputtering) by Amit Kanigel at Technion in Israel, for comparison. The magnitude and temperature dependence of the superfluid density are sensitive to critical fluctuations in the superconducting order parameter, both thermal and quantum. We find that severely underdoped Bi-2212 sustains strong, two-dimensional critical quantum fluctuations, indicating that the $T = 0$ phase transition from superconducting to insulating is a quantum critical point. A paper has been submitted to *Physical Review Letters*. (A poster presented at LT-26 in Beijing won “Best Poster” against more than 100 other posters on superconductivity.)

Second, we are working to grow ultrathin Bi-2212 films to see whether 2D critical thermal fluctuations appear, as they should and as they do in ultrathin $YBa_2Cu_3O_{7-y}$. We've achieved superconductivity in films as thin as 60 Å. Also, we are making other transport measurements like resistivity and Hall coefficient.

Third, for fundamental and practical reasons we studied the superfluid density of films of the iron-pnictide, $Ba(Fe_{1-x}Co_x)_2As_2$, grown at U. Wisconsin by C.B. Eom. We find that the T-dependence of superfluid density is dominated by a single superconducting gap, which is about half of the BCS value. Because measurements of other parameters reveal the presence of large and small gaps on different Fermi surface sheets, the question arises as to why the larger gap is absent from the superfluid density. On the practical side, our measurements showed that thin films are comparable in quality to single crystals. This work was published in *Physical Review B*.

Finally, we have been working successfully to improve our deposition protocol for ultrathin films of $YBa_2Cu_3O_{7-y}$. The present grant is focused on optimizing and studying these films in detail, so they must be as high quality as possible. Moreover, several other groups are interested in collaborating on these films and are doing measurements that we do not do, which again demands the highest quality, reproducible films.

We note that we spent a fair bit of time and effort on an unsuccessful study of ultrathin films of NbN supplied by a collaborator in Karlsruhe, Germany. We undertake high-risk high-reward projects, and some of them actually fail, verifying their high risk.

Optical Study of Spin Dynamics in Semiconductor Nanowires

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Funding:	$200,000

The central goal of this DOE project is to investigate spin relaxation behavior in quasi-1D semiconductor systems using time-resolved optical pump-probe techniques. In order to achieve this goal, the semiconductor nanowires must be able to absorb a circularly-polarized light for optical excitation of spin polarized carriers. Consequently, we have to overcome the optical polarization anisotropy originating from the quasi-1D geometry and the dielectric mismatch between the semiconductor nanowires and their environment, which can be achieved by coating the nanowires with a matching dielectric material of sufficient thickness.

We have been using pulsed laser deposition (PLD) to synthesize III-V semiconductor nanowires. We first demonstrated a general approach to ex situ dielectric matching to InP and ZnO nanowires by conformal coating of Ta_2O_5 using sputtering in order to reduce the optical polarization anisotropy. As a result, the polarization anisotropy is reduced by 86% for $InP:Ta_2O_5$ and 84% for $ZnO:Ta_2O_5$ due to the better dielectric matching (than air). This success validates a general scheme to control the optical polarization anisotropy and addresses a critical technical barrier to the use of polarized optical excitation to study spin dynamics in 1D nanostructures. This work was recently published in *Applied Physics Letters*.

Spin relaxation and optical properties in semiconductor nanowires are sensitive to defect states in nanowires. In order to understand the role of defect states in nanowires, we investigated the charge transport in PLD-grown n-InP nanowires using single nanowire field-effect transistor device. Temperature and gate dependent I-V measurements indicate a parallel transport channel due to surface trap states that shorts the band transport. These results highlight the complexity of charge transport in these materials and demonstrate the critical role played by defects in these quasi-1D structures. This work is currently under review at *Physical Review Letters*.

The preferred technique for III-V nanowire synthesis is metalorganic chemical vapor deposition (MOCVD) which not only offers the capability to grow nanowires with precisely controlled dimension, carrier type and concentration, but also enables synthesis of heterostructured nanowires with minimal surface defect states and dielectric matching. Using the new MOCVD at Ohio State, we have identified the optimal growth conditions for synthesis of GaAs nanowires epitaxially grown on GaAs substrates with essentially no tapering. However, bare GaAs nanowires show no detectable photoluminescence (PL), indicating high density of surface defects due to the exposed nanowire surface. By coating the GaAs nanowires with an $Al_{0.35}Ga_{0.65}As$ shell, we observed bright PL originating from the band edge emission of GaAs due to the fact that the AlGaAs shell passivates the surface of the core nanowires and essentially eliminates the surface trap states. The AlGaAs shell also provides an ideal dielectric matching. As expected, the PL of the core-shell nanowires with a thick AlGaAs shell exhibits essentially no polarization anisotropy, paving the way for spin dynamics studies in 1D semiconductors using pump-probe techniques. Recently, we overcame the technical challenges in optical measurements caused by the nanowire sample roughness and identified an optimal core-shell nanowire structure for time-resolved Kerr rotation measurements from the back of an etched hole in the substrate. This geometry allows for optical measurements of spin relaxation time on the section of GaAs nanowires with the highest quality and minimal level of defects.

Single Atom and Molecule Manipulation and Its Application to Nanoscience and Nanotechnology

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Funding:	$125,000

The ability to manipulate individual atoms and molecules with sub-atomic or single-bond level precision is critical in order to develop novel, power efficient, and smart nanoscale devices. In recent years, advances in scanning tunneling microscope manipulation of atoms and molecules have enabled probing the intrinsic properties of materials at the atomic level, building artificial quantum structures using individual atoms, and testing atom and molecule based nanodevices on a one atom or one molecule at-a-time basis. In the proposed research projects, we utilize the unique capability of scanning tunneling microscope atom/molecule manipulation schemes combined with tunneling spectroscopy to investigate a variety of novel nanoscale phenomena on atoms and molecules adsorbed on materials surfaces. Our research projects include nanoscale molecular superconductors, molecular level charge transfer processes, and development of atom/molecule manipulation techniques.

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

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Funding:	$80,000

The first main objective of this project is to probe the fundamental electronic and magnetic properties of nitride-based material systems, and in particular, specific bi-layer systems consisting of atomic layers of magnetic materials deposited onto semiconducting nitride surfaces. These include ferromagnetic metals, magnetic nitrides, and dilute magnetic nitride semiconductors. Such spintronic systems hold high promise as advanced materials for future energy-related applications. The second main objective of this project is to develop a strong U.S. effort in spin-polarized scanning tunneling microscopy. Based on the high level of activity involving unique instrumentation and research methodology, the principal investigator (PI) is well-positioned to accomplish these two objectives.

The PI has a history of accomplishment in the nitride materials field, beginning with the first proper identification of the two important families of surface reconstructions which occur on the basal plane surfaces of wurtzite gallium nitride – the (0001) and (000-1) faces – using scanning tunneling microscopy in 1997-99. Since 1998 at Ohio University, the PI has developed a full-scale research program to explore the fundamental properties of diverse classes of nitride systems, including semiconducting, magnetic, and spintronic nitrides. Furthermore, the PI also began a research program in spin-polarized scanning tunneling microscopy, achieving atomic-scale magnetic resolution of the antiferromagnetic surface Mn_3N_2 (010) already by 2002. This led to a series of articles and motivated the current project.

This DOE project involves both synthesis and analysis of magnetic and spintronic nitride materials. The experimental approach involves (1) epitaxial growth of selected magnetic nitride systems using molecular beam epitaxy and/or pulsed laser epitaxy and (2) investigation of these systems using in-situ scanning tunneling microscopy and spin-polarized scanning tunneling microscopy, as well as an array of additional characterization tools. Spin-polarized scanning tunneling microscopy is a uniquely powerful technique which measures the spin-polarized local density of states of a surface as well as the normal (non-spin-polarized) local density of states. By coupling this technique to a powerful growth facility via ultra-high vacuum, the intrinsic spin-polarization of a clean surface may be determined.

The work is carried out within the PI's two independent laboratories at Ohio University. The first laboratory is geared towards room-temperature, spin-polarized measurements under magnetic fields up to 1/2 Tesla, while the second is dedicated to low-temperature, spin-polarized measurements under magnetic fields up to 4.5 Tesla. This project is also enabling the PI to foster a strong and skilled research group involving graduate, undergraduate, and post-doctoral researchers.

This project will impact all possible magnetic and spintronic applications of nitrides. In each and every potential and promising application, it is essential to understand the fundamental nature of the spin-polarization of the magnetic/spintronic layer, down to the atomic scale, and in particular for thicknesses in the range 0-5 atomic monolayers. This is because of the critical nature of the magnetic states at the interface with the semiconductor. This DOE project addresses in a new way, long-standing questions about the origins of magnetism within dilute magnetic nitride semiconductors by atomically resolving the magnetic atoms and the spin states directly, and as a function of growth conditions. Finally, this project establishes a U.S. spin-polarized scanning tunneling microscopy research program capable of addressing challenging new problems in nanoscale magnetism and spintronics.

Manybody Effects in Chromium Thin Films

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Funding:	$160,000

The two primary foci of this project are as follows:

(1) Hydrogen impurities, localization, and magnetism in graphene. Predictions have existed for some time that that various species bonded to graphene, even H atoms, are magnetic. Our experiments involve cracking hydrogen molecules to produce H-atoms, which in turn bond at random locations on a graphene film grown on a SiC substrate. The electronic structure, in particular the coherence of the quasiparticle bands in the vicinity of the Fermi level, are then probed using photoemission as a function of hydrogen coverage/doping. We found direct evidence for a weak localization transition at a coverage close to where the minimum metallic conductivity is predicted.

(2) Electronic and magnetic structure of 1D atomic chains self-assembled on stepped single crystal surfaces. The properties of magnetic nanostructures are intensely studied at present due to their promise in emerging magnetic recording technologies. We grow nanowires and films of various atomic species (hydrogen, alkali metals, iron) on stepped tungsten surfaces. The electronic structure and Fermi contours of these systems is then measured using high resolution angle-resolved photoemission.

Approximately one year ago, I discussed with my BES program manager the possibility of closing this project down and initiating a new project focused on applications of coherent soft x-ray beams. The BES was supportive of this plan, and I did not submit a renewal proposal for this project. Instead, I submitted a proposal titled "Nanoscale Dynamical Heterogeneity in Complex Magnetic Materials.” This has been funded and is now being actively pursued. The project titled "Manybody Effects in Chromium Thin Films” was granted a no-cost extension, and that budget will be spent out in a few months.

Engineering of Mixed Pairing and Non-Abelian Quasiparticle States of Matter in Chiral P-Wave Superconductor Sr_2RuO_4

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Funding:	$100,000

The goal of the proposed research is to seek out the existence of novel 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 quasiparticles. Initial evidence for half-flux-quantum vortices, predicted theoretically to host non-Abelian Majorana modes, has been found in Sr_2RuO_4. However, 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 quantum states of matter.

We have focused on the search of half vortices by performing quantum oscillation measurements on small rings of Sr_2RuO_4 prepared by photo lithography and focused ion beam (FIB). In the bulk, the free energy associated with half vortices is usually higher than that of a full vortex because of the cost of spin-orbital coupling, except possibly in a narrow temperature range with magnetic field applied along the *ab* plane, or in small samples for which the spin-orbital energy cost is reduced by the finite sample size. Recently it was reported (J. Jang, D.G. Ferguson, V. Vakaryuk, R. Budakian, S.B. Chung, P.M. Goldbart, and Y. Maeno, "Observation of Half-Height Magnetization Steps in Sr_2RuO_4," Science 331, 186 (2011)) that the torque of a flux trapping doubly connected Sr_2RuO_4 sample of a mesoscopic size exhibited jumps corresponding to the flux change by the amounts of both Φ_0 and $\Phi_0/2$. The latter was only observed when the sample was subjecting to an in-plane magnetic field. It should be pointed out thathalf vortices were actually not observed directly in this experiment. Given that the control experiment carried out on similar samples made of conventional, *s*-wave superconductor $NbSe_2$ seems to have also revealed jumps corresponding to fractional flux changes, other experiments are needed to establish the existence of half vortices in Sr_2RuO_4 more fully. In this regard, the most direct observation may be direct imaging of half vortices, as done in the high-T_c tricrystal experiments (C.C. Tsuei and J.R. Kirtley, "Paring symmetry in Cuprate superconductors," Rev. Mod. Phys. 72, 969 (2000)). Alternatively, the observation of Little-Parks oscillations with a period of $\Phi_0/2$ will show that half flux quantum exists.

We explored a novel approach to make thin flakes of Sr_2RuO_4 by mechanical exfoliation using cleavable single crystals of Sr_2RuO_4 grown by a floating zone method by Professor Zhiqiang Mao of Tulane University. We developed photo and e-beam lithography and focused ion beam techniques to prepare Sr_2RuO_4 microstructures. To prepare such a device, contact leads of Ti/Au were prepared by photo lithography. Focused ion beam (FIB) was used to fabricate a ring of roughly 1 µm in diameter. We succeeded in fabricated superconducting rings of Sr_2RuO_4 with a diameter in the micron range. We observed beautiful quantum oscillations in several rings. The most prominent quantum oscillation was found to be that of a full flux quantum, Φ_0. Even though no $\Phi_0/2$ was observed, other interesting findings were obtained. A manuscript is being prepared to report these findings.

Exploration of Artificial Frustrated Magnets

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Funding:	$150,000

This proposal targets the study 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. Such geometrical frustration can lead to multiple energetically equivalent configurations for the magnetic moments of the islands and a variety of associated novel collective behavior. These systems are analogs to a class of magnetic materials in which the lattice geometry frustrates interactions between individual atomic moments, and in which a wide range of novel physical phenomena have been recently observed. The advantage to studying lithographically fabricated samples is that they are both designable and resolvable: i.e., we can control all aspects of the array geometry, and we can also observe how individual elements of the arrays behave. The proposed research combines a strong experimental effort, using both local probe and collective measurements, with theoretical modeling of these systems to allow a detailed understanding of the underlying phenomena.

In previous work, we have demonstrated that we can fabricate and probe frustrated magnet arrays, including some geometries that are directly analogous to the “spin ice” materials. We have designed frustrated lattices, controlled the strength of interactions by changing the spacing of the islands, and demonstrated that the island magnetic moment orientation is controlled by the inter-island interactions.

In the proposed research program, we plan several research thrusts to expand upon this initial effort, using both local and collective measurement techniques. We will investigate a range of frustrated lattice geometries in both small clusters and extensive arrays of islands, thus accessing a range of different types of frustration, each of which we expect to result in moment configurations that correspond to different accommodations of frustration. We will also examine how these systems respond to disorder, and we will vary the type of magnetic material from which the arrays are made. We will also probe the effects of both static and dynamic external magnetic fields. In related efforts, we will model the interplay of kinetics and effective thermodynamics in the manifolds of degenerate states of the island moment configurations.

In addition to shedding light on fundamental issues regarding frustrated magnetic systems, the study of these arrays will have connections to problems of technological interest in which arrays of locally interacting elements are fundamental to the design. For example, future information storage technology may use patterned recording media that consist of arrays of ferromagnetic elements. Although not designed to have interactions, the elements in these arrays will necessarily interact with each other due to the required high density and the long-range nature of the dipole interaction. Furthermore, prototypical logic devices have recently been fabricated which explicitly utilize the magnetostatic interactions of ferromagnetic islands. In a broader context, however, the flexibility in both the design and measurement of these arrays make them excellent model systems for studying complex phenomena that can emerge from simple interactions, and we expect that the results of the proposed research will have a far-ranging impact.

Studies of Interband Modes and Fermi Surface Features in Very Clean MgB_2 Films

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Funding:	$90,000

Distinct multi-band superconductivity is a unique feature that distinguishes MgB_2 from all other phonon-mediated Bardeen-Cooper-Schrieffer (BCS) superconductors. Besides the widely-observed two superconducting energy gaps arising from the s and p bands, theoretical calculations taking into account the fully anisotropic electron-phonon interaction further predict a distribution of gap values for both s and p bands on the Fermi surface of MgB_2. However, only two distinct gaps have been observed experimentally before. In this project, we studied electron tunneling spectroscopy on planner MgB_2/native oxide/Pb tunnel junctions grown on different substrates and orientations. We also vary the electron mean free path by introducing N gas during film deposition to introduce disorders in the films. The results clearly shows the distribution of energy gaps within one band in very clean samples for both bands, but the gap features become a narrow single gap as the mean free path is reduced. By deconvoluting the tunneling spectrum based on the density of state of Pb, we derive the momentum-dependent energy gaps of MgB_2, which are in good agreement with the anisotropic Eliashberg calculation. The result affirms the importance of the anisotropic electron-phonon interaction and Coulomb repulsion in MgB_2 and the energy gap values are not single value even within each band. We have also studied the angular dependence of magentoresistance as a function of temperature which reveals the multiband Fermi surface shapes and the interplay between the bands in electrical transport properties.

Development of Spintronic Bandgap Materials

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We propose to develop “spintronic bandgap materials” that will enable a rich variety of spin-based physical systems to be explored with an unprecedented degree of variation and control. Precisely defined patterns of sub-10-nm Ge quantum dots will be fabricated directly on silicon substrates. The small size of the Ge dots will enable single electrons to form bound states, and for nearest neighbors to interact via direct spin exchange. The “spintronic band structure” is determined by the geometrical arrangement of quantum dots and will be controlled using nanofabrication techniques recently developed by Levy and collaborators. The electronic and magnetic properties of these systems will be probed using capacitance spectroscopy and magnetic resonance force microscopy as a function of temperature (50 mK – 300 K) and magnetic field (14 Tesla). These exchange-coupled spin systems, formed from single electrons localized on the dots, can be mapped onto a wide class of interesting physical systems. These systems may also form the basis for quantum information processing architectures.

Long-Range Transport of Excitons in GaAs Quantum Well Structures

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Funding:	$120,000

This project focuses on excitons in coupled quantum well structures, also known as bilayer structures, which consist of two quantum wells adjacent to each other with a tunneling barrier between them. When an electric field is applied across the wells, spatially indirect excitons are formed, which have the electrons in one quantum well and the holes in the other quantum well. These excitons, also known as dipole excitons or indirect excitons, have a very long lifetime (up to 40 microseconds in our samples) and strong, long-range interactions. They are predicted to be superfluid at low temperatures, and in certain configurations have been predicted to make a new type of superconductor. Although excitons carry no net charge, their motion in the bilayer system can be put into a circuit which does carry charge.

Up to now, experiments claiming superfluidity of excitons in this type of system have been inconclusive; some claims have been made by other groups but are not widely accepted. Our group has focused on controlled trapping of the excitons. Under these conditions we have seen a new effect in which the luminescence of the excitons is effectively turned off at high density and low temperature. Some theorists have argued that this is evidence of superfluidity, or Bose-Einstein condensation, of the excitons in a dark (non-light-emitting) state. We have not claimed this, but we recently published a lengthy study of the effect in which we carefully looked at all the effects of stress and the band structure and showed that the effect cannot be simply explained by classical mechanisms.

In moving forward we have two thrusts. One is to use magnetic field to cause the dark exciton states to become able to emit light. This will allow us to directly observe the dark excitons which are predicted to be superfluid. These experiments are being done in collaboration with Alan Bristow at West Virginia University, a short drive from Pittsburgh.

Our second thrust is to make circuits with direct electrical contact to the quantum wells, using the fabrication facilities at the Peterson Institute for Nanoscience and Engineering of the University of Pittsburgh. These techniques were learned in an extended visit with Prof. Mansour Shayegan at Princeton University in January 2011. Because the dipole exciton gas is very strongly interacting, comparable to liquid helium in unitless terms, it may be that there is no clear spectroscopic signature for superfluidity from the exciton gas, but superfluidity will be observable in transport experiments. Similar experiments have already been done with excitons at ultralow (millikelvin) temperatures in a high magnetic field with doped bilayer structures. Our experiments will be at much higher temperature, where we still expect to see superfluid effects, since the excitons in our system are much more stable.

If our experiments succeed in showing superfluidity, it will open the door to seeing exciton superfluidity and superconductivity at room temperature, since excitons have a strong binding energy through the Coulomb interaction instead of the weak phonon-mediated interaction of Cooper pairs. Many existing systems have stable excitons at room temperature. Even at low temperature, this system would be a new class of superconductor which is superconducting only when exposed to light.

Magneto-Transport in GaAs Two-Dimensional Hole Systems

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Two-dimensional 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 other novel phases in the higher Landau levels. The goal of this project is to study the materials science and physics of ultra-clean two-dimensional electron and hole systems confined to modulation-doped GaAs/AlGaAs heterostructures. The samples are grown using the state-of-the-art technique of molecular beam epitaxy, and low-temperature magneto-transport measurements are used to explore their novel physics. Our studies include measurements of the transport properties of interacting carriers with spin and layer degrees of freedom; these are typically confined to single GaAs quantum wells of varying width or to double-quantum-wells of GaAs.

Probing Correlated Superconductors and their Phase Transitions on the Nanometer Scale

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PROJECTS FULLY SUPPORTED BY DOE-BES

(1) Physics of High-Tc Cuprates Superconductors—*Nature* (2010). Over the last number of years, each year our group has uncovered an important aspect of the physics of high-Tc cuprates using high precision measurements of the local electronic structure of these materials with the STM (Gomes et al. Nature 2007, Pasupathy et al. Science 2008). During the last two years, the team has focused on understanding the behavior of underdoped cuprates, at light hole doping concentration, which is important to determine how superconductivity emerges from a Mott insulating state. We have

demonstrated two important findings in this area. In a series of experiments (reported in Pushp et. al. Science 2009), we showed that that the pairing interaction in the underdoped samples (close to the Mott insulating ground state) is saturated in strength and demonstrated that the relative portion of the Fermi surface participating in the pairing interaction controls the superconducting transition temperature in this regime. These experiments illustrate that d-wave superconductivity emerges from the electronic state in specific part of the Fermi surface with the rest of the Fermi surface being tied up in exhibit in the so-called pseudogap behavior that competes with superconductivity. In the last year in another series of experiments (reported in Parker et al., *Nature,* 2010), we showed that the onset of pseudogap behavior which is precursor to superconductivity coincide with the appearance of real space electronic modulations that have predicted characteristics of fluctuating stripes. These experiments show that the pseudogap state is inherently unstable to make real space patterns of spin and charge that fluctuate. We show that as expected the strength of the stripe formation is maximal near hole concentration of 1/8 doping, as predicted by many numerical simulations. These experiments are the first to isolate the interplay between formation of stripes and pseudogap behavior in cuprates.

(2) Visualizing Kondo Lattice Behavior & Unusual Electronic Behavior of Heavy Fermion Systems—*PNAS* (2010). A remarkable variety of collective electronic phenomena have been discovered in compounds with partially filled f orbitals, where electronic excitations act as heavy fermions. Like other correlated electronic systems, such as the high temperature superconducting cuprates, several of the heavy fermion compounds display an interplay between magnetism and superconductivity, and have a propensity toward superconducting pairing with unconventional symmetry. During the last year our group has succeeded in application of scanning tunneling microscopy techniques to the study of heavy fermion systems. Our measurements provided a local perspective of Kondo lattice behavior in these compounds and have shown how this behavior is connected with novel electronic organizations in these compounds, such as the "hidden order" phase that forms in URu_2Si_2 compound. These experiments show the promise of scanning tunneling microscopy techniques to examine collective behavior of heavy electron system.

Our experimental program is unique in that currently no other experimental group has the STM capabilities to perform high-resolution experiments on correlated electronic states across the wide range of temperatures we can study. Overall, the real space information we have obtained from our experiments complements the scattering and ARPES studies supported under the DOE-BES program. Our experiments are done in collaboration with Professor Robert Cava's group at Princeton, with Dr. Genda Gu from Brookhaven National Laboratory, and Dr. Eric Bauer and Dr. Joe Thompson and Los Alamos National Laboratory.

PROJECTS PARTIALLY SUPPORTED BY DOE-BES BY SUPPORTING INFRASTRUCTURE AT PRINCETON NANOSCALE MICROSCOPY LABORATORY (support noted in publications):

(1) Topological Surface State—*Nature* (2010). Topological insulators are a new class of materials discovered to have unusually conducting surface states with Dirac-like energy dispersion and helical spin texture. Our group has been the first group to directly visualize these novel states with the STM and has demonstrated that these states are protected from backscattering due to their unusual spin texture. (Roushan et al., *Nature,* 2009) In another series of experiments, we have demonstrated that these surfaces not only do not back scatter, but they can penetrate through crystalline barriers that stops other surface states (Seo et al. *Nature,* 2010). These two experimental breakthroughs represent an important demonstration of the novel properties of topological surfaces that sets them apart from other two-dimensional surfaces that can be easily localized by disorder.

Visualizing Critical Fluctuation Near the Metal-Insulator Transitions—*Science* (2010). Electronic states in disordered conductors on the verge of localization are predicted to exhibit critical spatial characteristics indicative of the proximity to a metal-insulator phase transition. Such behavior is responsible for many of the unusual thermodynamic and transport properties of such systems, yet these fluctuations have never being directly examined in real space. Our group has used scanning tunneling microscopy to visualize electronic states in $Ga_{1-x}Mn_xAs$ samples close to the metal-insulator transition and have been able to show that their spatial variations are indicative of critical phenomena. (Richardella et al., *Science,* 2010) Near the Fermi energy, where spectroscopic signatures of electron-electron interaction are the most prominent, the electronic states exhibit a diverging spatial correlation length. Power-law decay of the spatial correlations is accompanied by log-normal distributions of the local density of states and multifractal spatial characteristics. Although these characteristics are very similar to those predicted for localization of non-interacting electrons, their connection with electronic signatures of interaction is rather important. Localization and metal-insulator transition are well-understood phenomena in the limit of weak interaction; however, its behavior in the interacting limit continues to be at the forefront of condensed matter physics.

Transport Experiments on 2D Correlated Electron Physics in Semiconductors

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Funding:	$165,000

The fundamental physics underlying the quantum Hall fluids is the strong interaction of the electron with other electrons and its interaction with the disorder in the electron system. It is the interplay of the disorder and interaction that gives rise to a host of novel quantum phases of the electron matter. The question whether the nature of the disorder matters has now been addressed in this research project. By comparing the energy gap of the 5/2 fractional quantum Hall effect (FQHE) state obtained in conventional high mobility modulation-doped quantum well samples with that obtained in high quality GaAs-AlGaAs heterojunction insulated-gate field-effect transistors, it is discovered that the roles the long-range and short-range disorders play in the stability of the quantum phase are different. The long-range potential fluctuations are more detrimental to the strength of the 5/2 FQHE state than the short-range potential fluctuations.

Experiments on Quantum Hall Topological Phases at Ultra-Low Temperatures

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The purpose of this project is to cool electrons in semiconductors to extremely low temperatures (1 millikelvin) 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 will open the door for fundamental discoveries in condensed matter physics. Understanding low-temperature electron transport in low-dimensional and nanoscale devices is the foundation for developing next generation quantum information and quantum computation technologies.

Brief overview of project in progress during FY 2011.

(1) We have performed the experiments of 5/2 fractional quantum Hall state under a small in-plane magnetic field; a paper based on the results from this experiment has been submitted to *Physical Review Letters*.

(2) We are in the process of purchasing the piezoelectric rotator to be used for the in situ sample rotation, and will install the device in the mK refrigerator.

(3) We have measured a new set of ultra high-mobility GaAs/AlxGa1-xAs quantum wells grown by Dr. Loren Pfeiffer of Princeton for the preparation of mK experiments.

(4) Additional data has been taken using 45T DC magnetic field in NHMFL for the high mobility, carbon-doped 2D hole QWs grown by Dr. Loren Pfeiffer of Princeton and Dr. Michael Manfra of Purdue. Under previous DOE support we have discovered a Wigner crystal in this new material, which shows very interesting sliding to insulating conductivity transition as a function of temperature. We are writing up the paper.

(5) Graduate student Ivan Knez has been doing research in quantum spin Hall effect in InAs/GaSb composite QWs. Part of his efforts is to fabricate Nb-InAs/GaSb junctions, and measure their low temperature transport. Although this topic is not in the fractional quantum Hall effect area, its' underlying physics is connected to the topological quantum phases at 5/2. Knez is 50% supported by the DOE grant.

Nanostructure Studies of Strongly Correlated Materials

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Funding:	$115,000

Materials with strong correlations between the electrons are some of the richest in condensed matter physics and materials science. These strongly correlated electronic systems (SCES) often exhibit dramatic phenomena, including metal-insulator transitions, magnetic and electronic ordering, and high temperature superconductivity. In this project we leverage nanostructure techniques, developed over the last two decades in studies of metals and semiconductors, to examine the underlying physics in these materials. Nanostructure methods allow the examination of SCES on length scales comparable to their intrinsic or extrinsic inhomogeneities, and enable the application of large electric fields as perturbations without large charge carrier energies. The two materials systems we are examining most thoroughly are Fe_3O_4 (magnetite), and VO_2 (vanadium dioxide). Both materials have high temperature metallic states separated from low temperature insulating states by combined electronic and structural phase transitions. In both systems, the role of electronic correlations in the metal-insulator transition is hotly debated. In magnetite, we have found that a large electric field can destabilize the insulating state, leading to a nonequilibrium transition to a more conducting state. We are currently examining the role of magnetic field in altering this nonequilibrium transition, as well as looking at ionic gating as an alternative means of applying such a large electric field. In vanadium dioxide, we have attempted to use ionic liquids as a means of gating the metal-insulator transition. Surprisingly, there is no detectable gating effect despite the large inferred surface charge density in the individual VO_2 nanowire devices. However, we have discovered as a result of this work that it is possible to dope VO_2 micro- and nanocrystals reversibly with atomic hydrogen. In particular, using catalytic spillover, we have been able to stabilize a (distorted) form of the high temperature, metallic, rutile structure all the way down to cryogenic temperatures. We are currently investigating the physics of this remarkable stabilization, and the properties of and role of electronic correlations in the newly stable metallic state. This work has supported a graduate student and has had a postdoctoral researcher (supported by non-DOE fellowship funds) contributing. We believe that we have only begun to realize the full potential of nanostructure-based methods as tools for studying and engineering the basic physics of this diverse family of materials.

Spectroscopy of Degenerate One-Dimensional Electrons in Carbon Nanotubes

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Funding:	$150,000

We are studying the fundamental properties of degenerate one-dimensional (1-D) electrons in single-walled carbon nanotubes (SWNTs) using dynamical methods to probe and understand electronic correlations and many-body phenomena. SWNTs are an ideal 1-D system for studying novel quantum effects in nanostructures. There have been transport and optical studies on SWNTs 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.

Near-Field Raman Scattering of Carbon Nanotubes

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We study the influence of defects and dopants on the physical properties of carbon nanotubes and graphene. 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.

Experimental Studies of Magnetic Correlation and Induced Superconductivity in Graphene Crystals

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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 proposed research will explore the emergence of new physical phenomena and the feasibility of devices based on the unique charge carriers in graphene. It will address basic questions about the properties of graphene and about the nature of its charge carriers, addressing such questions as: (1) What is the role of interactions? (2) Can one observe new phases in a magnetic field including fractional quantum Hall effect and broken symmetry phases? (3) What is the interplay between massless Dirac fermions and Cooper pairs at the boundary between graphene and a superconductor? We will investigate the feasibility of devices based on superconductor/graphene/superconductor junctions. 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.

Raman Spectroscopy of Iron Oxypnictide Superconductors

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High-resolution electronic Raman scattering has become an indispensable tool in the arsenal for understanding many-body physics and allowing for the study of magnetic, electronic, and other collective phenomena. Electronic Raman scattering has played a major role in characterizing the anisotropic dynamics of electrons across the phase diagram of cuprate superconductors. This includes the study of antiferromagnetism, where Raman measurements on the parent insulating cuprate compounds yielded an estimate of the magnetic exchange interaction strength from the energy of the two-magnon scattering. Raman spectroscopy has provided new insights into unconventional superconductivity, including the symmetries of the superconducting order parameters, the nature and properties of the in-gap collective modes, and clear signatures of the multi-band effects. One of the most illustrious achievements of polarized electronic Raman scattering has been the ability to focus on the nature of electron dynamics in different regions of the Brillouin zone in which charge excitations can be selectively mapped and analyzed using group-theoretical symmetry arguments. This distinguishes Raman scattering from most other transport and thermodynamic measurements, allowing for the study of the development of correlations in projected regions of the Brillouin zone.

The objectives of this project are to investigate the manner in which charge, spin and lattice coupling, and dynamics evolve through various low-temperature, doping-concentration and high-magnetic-field phases of newly discovered iron oxypnictide superconductor materials by employing magnetic-field-tuned low-frequency electronic Raman (i.e., inelastic light scattering) spectroscopy, and to clarify the microscopic origin of unconventional superconductivity and magnetism in these compounds. We propose electronic and magnetic Raman spectroscopic study of the oxypnictide compounds across the phase diagram as a function of carrier concentration, temperature, and magnetic field with the following goals: (1) by analyzing two-magnon Raman scattering for parent and lightly doped oxypnictide compounds, establish the evolution of magnetically ordered state; from the interpretation of resonant two-magnon scattering bands, make a quantitative estimate of the exchange interaction strength as function of doping and temperature; (2) evaluate the interplay between structural, magnetic, and superconducting transitions from systematic phononic, magnetic, and electronic polarized Raman scattering study as a function of doping, temperature, and magnetic field; (3) examine the symmetry of the superconducting order parameter, the magnitude of the superconducting gaps and their evolution with doping from polarized ultra-low-frequency electronic Raman scattering; (4) study the evolution of superconductivity with magnetic fields and determine the upper-critical fields and superconducting correlation lengths as functions of doping by magneto-Raman scattering experiments; and (5) search for the novel collective modes expected in the superconductors with multiple condensates and study their systematics. Among the anticipated outcomes of this project are (1) the 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) the determination of a complete spectrum of collective excitation for the new family of unconventional multi-band superconductors driven by magnetic interactions.

Transport Behavior of Superconductors at High Dissipation and Short Timescales

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The Kunchur group investigates novel phenomena and properties of superconductors under extreme conditions. The electromagnetic transport response is measured at unprecedented power densities--exceeding a billion watts per cubic centimeter--and short time scales. When a magnetic field is applied to a (type II) superconductor, it produces quantized flux vortices within the superconductor. This is referred to as the mixed state of a superconductor. In this group's prior work, new phenomena were discovered as the vortices were pushed to extreme (even supersonic) speeds. In current ongoing work during 2011, a new regime is being investigated in which the vortex becomes strangled and explodes as the sample thickness become small compared to the size of a vortex and chokes it out of existence. This effect was theoretically predicted by Likharev but had not been observed before. The state above the vortex explosion transition shows an unusual exponential magnetic-field dependence of resistance, a behavior that has not been seen before. The nature of the state above the explosion transition is not currently understood and this matter is under further investigation. This study is expected to have practical implications for photon detectors.

Spectroscopic Investigations of Novel Electronic and Magnetic Solids

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Funding:	$135,000

The Musfeldt research group is interested in the behavior of materials under extreme conditions. We are well-known for our spectroscopic work in high magnetic fields, under unusual chemical and photo-chemical activation, and at very small sizes where quantum confinement effects become apparent. 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. Current efforts include (1) investigating magnetic field-induced color changes in model oxides like α-Fe_2O_3, (2) understanding spin-spiral quenching in rare-earth substituted-$BiFeO_3$ where combined ferroelectricity and ferromagnetism exists in a narrow substitutional range, (3) probing magnetic quantum critical systems like $Mn(dca)_2$ where the field-driven transition amplifies magnetoelastic coupling, and (4) investigating nanoscale oxides like MnO and $CoFe_2O_4$ where spectral analysis reveals size-dependent changes in chemical bonding, magnetoelastic coupling, and core-shell structure. 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.

Emergent Behavior in Magnet-Superconductor Hybrids

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Funding:	$150,000

We study emergent behaviors which appear when two mutually exclusive states of matter, superconductivity and magnetism, are combined at the nanoscale in a unified system.

The year 2011 completes a century of superconductivity (SC) discovery. It is now experiencing a renaissance associated with advances in nanotechnology. Among of the most promising of new materials are Ferromagnet-Superconductor Hybrids (FSH). This field, started about ten years ago (by the present PI's among other researchers), has matured with dozens of research groups around the world and several topical conferences. From the very beginning of the current project we have focused our efforts on fabricating arrays of nanomagnets with the smallest possible features and strongest possible fields. The inhomogeneous magnetic fields, created by nanostructures, have been used to pin vortices in superconducting films. With an order of magnitude stronger fields and smaller size than used in previous studies, we were able to increase the magnetic field range for a strong critical current by an order of magnitude. The critical current increase for different external magnetic field strengths varied from a few times to a several orders of magnitude.

This research will result in (1) development of fabrication techniques for the new class of FSH systems, (2) development of understanding emergent behavior in systems with mutually exclusive states, (3) development of better understanding of pinning of vortices and Cooper pairs by magnetic nanostructures, and (4) education in modern methods of nanofabrication, materials characterization and studies of emergent behavior for graduate and undergraduate students.

Optical and Electrical Properties of III-V Nitrides and Related Materials

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Funding:	$158,000

High Al-content AlGaN alloys, covering wavelengths from 300 to 200 nm, are ideal materials for the development of chip-scale deep ultraviolet (DUV) light sources/sensors. Although tremendous progress has been made, improving material quality and fundamental understanding of basic properties of Al-rich AlGaN alloys as well as pure AlN remains the most outstanding challenge. Time-resolved DUV photoluminescence (PL) together with other optical and transport measurements have been employed to study optical and electrical properties of AlGaN and AlN epilayers. The focus was to achieve a better understanding of the band structures, properties of fundamental and defect optical transitions and carrier dynamics, and the roles of native defects such as cation vacancies in III-nitrides. The effects of Si-doping on the structural and optical properties of AlN epilayers have been investigated. Our studies revealed that that the accumulation of tensile stress in Si-doped AlN is a reason for the formation of additional edge dislocations and that the line-widths of both band-edge and impurity related transitions are directly correlated with the density of screw dislocations, which increase with an increase of Si-doping concentration. The results thus established that PL can be utilized as a nondestructive and highly effective method to characterize the relative dislocation densities in AlN. Our PL studies indicated that the origin of the yellow and amber color in bulk AlN is due to a band-to-impurity absorption involving the excitation of electrons from the valence band to the doubly negative charged state of isolated aluminum vacancies. The yellow coloration in AlN bulk crystal limits the UV transparency and hence restricts the applications of AlN substrates for deep UV optoelectronic devices. By knowing its origin, it is possible to eliminate the yellow coloration in bulk AlN by minimizing the concentration of isolated aluminum vacancies.

DUV PL spectroscopy has been employed to investigate the exciton-phonon interaction in AlN. Longitudinal optical (LO) phonon replicas of free exciton recombination lines were observed in PL emission spectra, revealing the coupling of excitons with LO phonons (110 meV). We have quantified such interaction by measuring Huang–Rhys factor based on polarization resolved DUV PL measurements. It was observed that the exciton-phonon coupling strength in AlN depends on the polarization configuration. Furthermore, a larger coupling constant was also measured in AlN than in GaN. We believe that the large effective hole to electron mass ratio in AlN mainly accounts for the observed results. We have also explored the potential of AlInGaN quaternary alloys as high temperature thermoelectric (TE) materials. It was found that the incorporation of erbium (Er) introduces nanoparticle-like phonon scattering centers to further reduce the thermal conductivity, while co-doping with Si was necessary to achieve n-type conductivity control. The temperature-dependent TE properties were measured up to 1055 K for an Er and Si co-doped n-type Al0.1In0.1Ga0.8N alloy. The figure of merit (ZT) showed a linear increase with temperature and is about 0.3 at 1055 K. The ability to survive such high temperature with reasonable TE properties suggests that low In-content Er and Si-doped AlInGaN alloys are potential candidates of high temperature TE materials. In addition to their well established outstanding physical properties for electronic device applications (the ability for high temperature/high power operation and radiation hardness), our initial results indicated that III-nitrides have great potential for TE power generation in high temperature environments. High temperature TE devices offer great potential for waste heat scavenging from power plants and the exhausts of automobiles and aircrafts due to their ability to directly convert heat to electricity.

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

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Efficiently harvesting, modulating and transporting light energy is a central feature of technologies ranging from photovoltaics to telecommunications. The objective of our project is to understand the way that energy delivered by photons to both metals and insulators can be stored, manipulated and exchanged in material structures with characteristic feature sizes smaller than the wavelength of the incident photons. In our project, the key physics idea is to use a wide variety of light sources to understand the coupling of excitons (the electron-hole pairs created by the absorption of a photon in an insulator) and plasmons (the collective oscillations of electrons in a metal). To meet our objectives, we use a combination of nanofabrication, microscopy and time- and space-resolved spectroscopies, coupled to powerful computational and analytical tools.

For example, we showed how to use the plasmonic response of gold nanoparticles to measure ultrafast acoustics in alumina superlattices; used plasmonic structures as nano-antennas to probe the metal-insulator transitions in a correlated-electron material (VO_2); tracked a structural phase transformation in VO_2 nanoparticles by surface-enhanced Raman scattering; and explored the unusual optics of a completely unsymmetric plasmonic structure, the nanoscale Archimedean spiral. We also measured the space and time dependence of exciton-plasmon coupling in material structures comprising zinc-oxide quantum wells and metal nanostructures, designed to allow ultrafast energy exchange and continuous tuning from the weak- to the strong-coupling regimes.

The interdisciplinary projects envisioned for the next three years emphasize (1) optical processes in “designer” nanostructures where plasmonic functionality is controlled by phase transformations (e.g., the insulator-to-metal transition in vanadium dioxide) or geometric constructions such as spirals inside rings and (2) ultrafast dynamics in structures designed to exhibit more efficient coupling and energy-transfer mechanisms between excitons and plasmons. These thematic groupings emphasize connections between optical and materials physics, on one hand, and ultrafast photon, electron and phonon dynamics in nanostructured materials, on the other.

The new projects capitalize on our work during the last 3 years and include (1) new laboratory capabilities in femtosecond laser spectroscopy; (2) confocal Raman microscopy that, combined with nanoscale lithography, allows us to image single nanoparticle; and (3) nanoscale materials fabrication (dual-layer electron-beam lithography, quantum-well fabrication, multilayer sputtering, focused ion-beam nanomachining). The experiments are both guided and analyzed by extensive computer simulations running on lab-built multi-core processors. In this “vertically integrated” research strategy, graduate and undergraduate students are trained in all aspects of their projects, from material fabrication and characterization through spectroscopy, simulation and analysis.

Ultrafast Studies of Hydrogen and Related Defects in Semiconductors and Oxides

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Funding:	$200,000

This last year we have focused on opto-acoustic studies of Ne^{++} ion irradiation in GaAs, which has provided an understanding of the fundamental interaction between crystalline disorder in semiconductors and the resulting optical modifications. We were able to estimate the number of atoms per unit radiation damage whose optical properties were modified via lattice strain at nearly ~700 atoms, which gives rise to the enhanced sensitivity of the CAP technique to crystalline disorder versus microscopy techniques or ion channeling analysis. These results have been submitted to Physical Review B and are currently under review. We are utilizing our understanding gained from the GaAs studies and extending it to other novel material systems. Also, in the last year, we have studied the properties of H in SnO_2 single crystals with infrared spectroscopy. When H or D is introduced into SnO_2 by annealing in an H_2 or D_2 ambient at elevated temperature, several O-H and O-D vibrational lines are produced along with the low-frequency absorption that is characteristic of free carriers. To probe the relationship between H and the free carriers it introduces, the thermal stability of the free carrier absorption and its relationship to the thermal stabilities of the O-H lines have been examined. Two H-related donors are found, one that is stable at room temperature on a time scale of weeks and a second that is stable up to 600°C. These electrically active defects are found to interact with other O-H centers and can be converted from one to another by thermal treatments. The oxide work is done in collaboration with Prof. Michael Stavola at Lehigh University, and Dr. Lynn Boatner at Oakridge National Laboratory.

Spin-Coherent Transport Under Strong Spin-Orbit Interaction

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The project aims to gain fundamental insight into spin-dependent quantum coherent phenomena arising from spin-orbit interaction, via experiments on nanolithographically prepared solid-state samples. The ultimately magnetoelectric phenomena studied under the project also have long-term significance in solid-state technology. The experiments use electronic transport in structures with mesoscopic length scales, namely approaching the mean free path and the quantum phase- and spin-coherence lengths. Such length scales will be relevant in future magnetoelectronic and spintronics devices, and presently allow a unique understanding of coherent spin-dependent electronic processes. Moreover, under spin-orbit interaction the electric fields confining the carriers within the edges of the mesoscopic structure interact with the spin degree of freedom, a subject of growing fundamental and applied interest. A deeper understanding of incompletely understood spin phenomena and quantum interactions in solids is indispensable to ultimately develop new electronic and magnetic device functionalities.

Objectives of the project include the measurement and characterization of a distinctive spin phenomenon, the Aharonov-Casher quantum-mechanical phase, and its associated vector potential. The Aharonov-Casher phase is the electromagnetic dual of the Aharonov-Bohm phase, obtained by exchanging the magnetic fields and electric charges that appear in the Aharonov-Bohm phase by electric fields and magnetic moments (spin) respectively. Similarly to the Aharonov-Bohm phase, the Aharonov-Casher phase has deep implications, and yet the experimental study of Aharonov-Casher quantum mechanical effects in the solid-state is at the early stages. The objectives comprise studying the consequences of the Aharonov-Casher phase and vector potential generated by the confining electric fields defining the boundaries of a mesoscopic spin-coherent sample, and by the spin-orbit interaction in the materials. The study uses semiconductor systems where the spin-orbit interaction is strong and where quantum coherence is manifest at low temperatures: two-dimensional electron systems in quantum wells of the narrow-bandgap semiconductors InAs, InGaAs, and InSb. The objectives also include a study of the elemental semimetal bismuth and of its strongly spin-orbit coupled surface states. Bismuth as an electronic material has recently yielded unanticipated magnetotransport data, yet is relatively unexplored as a material for phase-coherent and spin-coherent thin film mesoscopic structures. Objectives hence also include 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.

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

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Funding:	$150,000

Multiferroic, magnetoelectric heterostructure systems have recently attracted great research interest, due to their potential application in multifunctional devices, such as magnetic memories, sensors and spintronics. Indeed, impressive progress has been made, such as the fabrication of room-temperature multiferroic heterostructures, and the observation of a four-state resistance state in a multiferroic tunneling junction. However, most of these studies cannot reveal the important underlying physics behind the coupled ferromagnetic and ferroelectric order at the heterointerfaces, which obviously plays a crucial role in determining multifunctional behavior. Our experimental techniques, Magnetic Second Harmonic Generation (MSHG) and Time Resolved Magneto-Optic Kerr Effect (TRMOKE), can provide a direct probe of the magnetic state and spin dynamics at the heterointerface, and hence turn out to be effective tools to investigate this ME coupling. We plan to measure with MSHG the variance of hysteresis loop and magnetic anisotropy at the interface of multiferroic heterostructures under different applied electric fields. Electric field-modulated spin dynamic behavior of such system will be probed by TRMOKE which will provide information on spin pinning centers at the interface. We expect to see variances of the pinning state and the distribution of spin population at the interface by applying different electric fields.

Atomic Layer Controlled Growth of Pnictide Thin Film Heterostructures by Design

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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. Recently, we reported novel template engineering using single-crystal intermediate layers of (001) $SrTiO_3$ and $BaTiO_3$ grown on various perovskite substrates. This has enabled genuinely epitaxial films of Co-doped $BaFe_2As_2$ with superior J_c of 4.5 MA/cm^2 (4.2K) and strong c-axis flux pinning. We also demonstrated low anisotropy $\gamma<2$, strong vortex pinning, a high irreversibility field H_{irr} (close to H_{c2}), and critical fields of H_{c2} well over 50 T.

Our advance in pnictide single-crystal film growth allows the design and control of pnictide superconducting films and heterostructures to probe the fundamental superconducting mechanisms of this unique class of materials. 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

(4) Pnictide grain boundary engineering

The proposed work is based on a new growth technique with the unique potential for pnictide heterostructure synthesis with atomic-level control. Scientifically, we will learn how atomic scale positioning of interfacial layers modify the growth modes, epitaxial arrangements, and strain states. Technologically controlled growth of pnictide thin films and heterostructures through interfacial engineering will lead to the discovery of new superconducting structures and devices. In addition, the template technique that permits high-quality pnictide films on oxide substrates will likely be useful in interfacing other metallic or semi-metallic systems with oxides.

DOE National Laboratories

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

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Funding: $2,234,000

Humanity’s quest for materials with better properties is so integral to the fabric of its history that epochs are named after the materials that define them: stone, bronze, iron, and silicon. Currently humanity is desperately trying to develop materials that will allow for improved generation, transport, and even storage of energy. Among these materials, compounds that exhibit correlated electron states, emergent phenomena, and/or superconductivity have great promise but also great difficulties that need to be overcome: problems associated with our need to reliably find, understand, improve, and control these promising ground states. New systems are needed both for better properties and for providing further experimental insight that, in turn, can inform and inspire better theoretical understanding. With such systems and understanding, we hope to manipulate and control superconducting, magnetic, thermoelectric, and other properties so as to address humanities pressing energy needs. To this end, the specific scientific goal of this FWP is to develop, discover, understand, and ultimately control and predictably modify new and extreme examples of complex states, emergent phenomena, and superconductivity.

Photonic Systems

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Funding: $693,000

This FWP focuses on the design, fabrication, and properties of photonic crystal structures (PC) and the photophysics of luminescent organic semiconductors and organic light-emitting diodes (OLEDs). In this project we aim to control the flow of light and the conversion of light energy into other forms of energy (and vice versa) through the use of artificially designed and fabricated structures. Two of the most exciting and promising developments in physics and engineering are (1) the endowment of photons with revolutionary propagation and spectral properties, through their interaction with novel artificial structures, and (2) the emergence of organic semiconductors and organic electronics. In this FWP, we continue and integrate these two thrusts. Our overall strategy is to explore the new physics enabled by photonic structures and organic semiconductor materials and devices, both theoretically and experimentally, and to examine the impact of photonic structures and organic semiconductor materials and devices in areas supporting the mission of DOE in energy-efficient lighting, efficient solar energy utilization, thermophotovoltaics, and novel sensors. We will investigate the behavior of organic semiconductors and photonic structures incorporated into devices in these areas, in particular organic devices. We will leverage our work with our expertise in simulation, design, and fabrication of photonic structures as well as our experience in OLEDs developed in our previous studies under DOE. Over the last 5 years, we have developed a patented economical in-house soft-lithographic method for fabrication of three-dimensional polymer molds. These molds are then coated or backfilled with metal or dielectric materials to achieve three-dimensional (3D) micro- and nano-structures structures with the desired optical properties. In addition to work within the FWP, we also work with other external groups, worldwide to explore new functionalities enabled by new photonic structures. In the study of luminescent organic semiconductors, π-conjugated thin films are studied by photoluminescence and photoinduced-absorption-detected magnetic resonance and the operation of OLEDs fabricated in our experimental group is studied by electroluminescence- and electrical-current-detected magnetic resonance measurements.

Surface Structures Far-From-Equilibrium

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Funding: $578,000

Phenomena on the nanoscale can be very different from phenomena in the bulk. Either because of dangling atomic bonds at corners and edges of the nanostructure, or because as quantum mechanics becomes more important on the nanoscale, unexpected effects and properties emerge. One of the goals of this FWP is to discover robust ways to grow surface-supported nanostructures with less than ~1000 atoms (nanoislands, nanodots, nanowires etc.) with controllable dimensions (height, size, shape) and morphology (flat-top, wedding cake, stepped etc). This requires a better understanding of the many atomistic processes that determine how atoms diffuse and build and retain these structures. The project partly builds on the fact that metallic islands can be grown of identical “magic” height because quantum mechanics requires the confined electrons to “fit” only certain heights. A different goal is to use these custom-made, controllable nanostructures to enhance the rate of atomistic processes (nucleation, adsorption) and the yield of chemical reactions (that do not occur or have low rates on surfaces of bulk materials). We are currently pursuing molecular hydrogen adsorption on Mg nanostructures (which does not absorb on bulk Mg crystals) and adsorption of oxygen and hydrocarbons (relevant to ethylene oxidation) on Ag nanostructures.

Digital Synthesis: A Novel Pathway to New Collective States in the Complex Oxides

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Funding: $410,000

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, bismuthates, and cuprates, where the effects of disorder have been engineered away by digital synthesis. We will use the electric field-effect and currents to manipulate collective states in heterostructures. The electric field-effect permits ‘doping’ of charge at an interface, either capacitively or via a ferroelectric polarization, without introducing disorder. Electric currents can create a spin torque in magnetic materials. We seek to create and discover materials that are on the verge of a transition and tune these with the electric-field effect and currents. Lastly, we will explore a new class of materials, the iridates, where strong spinorbit interactions play a definitive role. This leads to novel correlated insulators, and superconductors and topologically protected surface states have been predicted in these materials. 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.

Emerging Materials

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Funding:	$1,345,000

New materials are the gateway to new phenomena, a better understanding of known phenomena, and performance enhancements. Our group couples materials synthesis tightly to insight-driven science as the most efficient pathway to breakthrough results. Within this synthesis-science dyad, our program will broaden its horizons beyond our high-impact 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 in the 3d systems.

Inspired by the novel Mott state recently identified in the nominally $J_{eff} = ½$ state of Sr_2IrO_4, we will 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 will explore metal insulator transitions in the presence of this entanglement and search for links to unconventional superconductivity. We will create 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 will use reduced dimensionality to test the generality of magnetic and electronic phase segregation; and we will explore 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.

Magnetic Thin Films

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Funding: $1,990,000

The hot issues that our group will address 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 will provide insights into artificial magnonic materials. The proposed work will advance our fundamental understanding of linear and nonlinear excitations in magnetic nanostructures. Our program in spin transport focuses on the physics of pure spin currents. It is only recently that spin currents have been recognized as a possible means to communicate without charge currents, potentially eliminating some of the wasted heat that impedes further transistor miniaturization. Due to this heat, information technology is becoming 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 nanomagnetic composites with low or no rare-earth content than can still exceed today's commercial capabilities as used in electric motors and generators, or ferromagnetic-superconducting multilayers that support an exotic interfacial pairing mechanism 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 materials explored within this proposal also provide samples worthy of advanced characterization at BES major characterization facilities.

Superconductivity and Magnetism

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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 Challange pursuit is devoted to the new iron pnictides, which embody a new opportunity in the search for an isotropic high temperature superconductor. Another Grand Challange pursuit 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 also seeding promising new research into the spectral character of THz radiation from high temperature superconducting crystal micro-mesas, 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 superconductivity in iron pnictide superconductors, (2) developing nano-pinscapes to control vortex pinning and vortex liquid flow, (3) investigating complex phenomena at the interface of superconductivity and magnetism in innovative hybrid heterostructures, and (4) elucidating the physics of coherent THz electromagnetic wave generation by intrinsic Josephson junctions in crystal micro-mesas.

Atomistic Transport Mechanisms in Reversible Complex Metal Hydrides

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Funding: $700,000

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.

In this collaborative research project, 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.

The impact of this program will be to provide a comprehensive understanding of the role of dopants and of complex reaction environments in facilitating the hydrogenation and dehydrogenation of Al-based hydrogen storage materials, including complex metal hydrides and light metal hydrides.

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

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Funding:	$550,000

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 the research described here. 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 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.

We are seeking new families of Fe-based compounds that can be tuned compositionally or by magnetic fields to a quantum critical point, where magnetic order is only possible for T=0. We synthesized high quality single crystals of the XFe_2Al_{10} compounds (X=Y,La,Lu). All of these compounds are metallic, but none order magnetically. YFe_2Al_{10} has strongly enhanced susceptibility and specific heat, indicating proximity to a ferromagnetic quantum critical point. Magnetic fields tune YFe_2AL_{10} away from this quantum critical point, and restore conventional Fermi liquid properties, albeit with a quasiparticle mass that diverges as the field approaches zero. We have also synthesized single crystals of $FeGa_3$, which is an insulator, possibly as the result of strong interactions. An insulator-metal transition can be driven by replacing Fe with Co, driving a simultaneous antiferromagnetic quantum critical point. A primary goal of our FWP is to seek unconventional superconductors near quantum critical points in iron-based Heusler compounds. We have succeeded in synthesizing high quality single crystals of two Heusler systems of interest, Fe_2VAl, and Fe_2TiSn, both of which are thought to be half-metallic. This has not been accomplished previously, and it is an enabling step for our magnetization, specific heat, and electrical transport measurements that will study the metallic state and its instabilities, to determine whether quantum criticality is decisive in these systems. We have begun collaboration with the group of P. Johnson that is aimed at studying the evolution of the Fermi surface in these compounds, as they are compositional tuned through magnetic instability at the quantum critical point.

Electron Spectroscopy

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Funding: $1,800,000

The program's primary focus is on the electronic structure and associated dynamics of condensed matter systems. The group carries out studies on a range of materials including strongly correlated systems. A special emphasis is placed on studies of high Tc superconductors and related materials. 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 Department and at the National Synchrotron Light Source. The emphasis is on the study of the low energy excitations and the nature of the interactions of the latter with their environment.

In FY 2011, the optical properties of the iron-chalcogenide superconductor FeTe0.55Se0.45 have been examined along the c axis. In the normal state the c-axis response is incoherent and is similar to the c axis of moderately underdoped cuprates. The incoherent response is found to be related to the strong dissipation in the a-b planes, a pattern that is found to be true for many other correlated electron systems as well.

The optical properties of the heavy Fermion URu_2Si_2 have also been examined in a number of different laboratories, allowing new high resolution, low-noise data to be obtained above and below the hidden-order transition at ~17 K. In the normal state, above the hidden-order transition, the optical resistivity can be generalized to a Fermi-liquid like with a dependence on frequency and temperature. Comparison with dc transport measurements indicate that intrinsic strong elastic scattering dominates, resulting in an unconventional, the term "Fermi molasses" has been coined to describe this incoherent Fermi liquid.

Electron emission from the negative electron affinity (NEA) surface of hydrogen terminated, boron doped diamond in the [100] orientation has been investigated using angle resolved photoemission spectroscopy (ARPES). ARPES measurements using 16 eV synchrotron and 6 eV laser light are compared and found to show a catastrophic failure of the sudden approximation. While the high energy photoemission is found to yield little information regarding the NEA, low energy laser ARPES reveals for the first time that the NEA results from a novel Franck-Condon mechanism coupling electrons in the conduction band to the vacuum.

High-resolution spin- and angle-resolved photoemission studies have been carried out on the electronic structure and the spin texture on the surface of Bi_2Se_3, a model Topological Insulator. By tuning the photon energy, it was found that the topological surface state is well separated from the bulk states in the vicinity of kz=Z plane of the bulk Brillouin zone. The spin-resolved measurements in that region indicate a very high degree of spin polarization of the surface state, ~0.75, much higher than previously reported. The results demonstrate that the topological surface state on Bi_2Se_3 is highly spin polarized and that the dominant factors limiting the polarization are mainly extrinsic.

Spectroscopic Imaging STM for Complex Electronic Matter Studies

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Funding:	$320,000

VISUALIZING THE CREATION OF HEAVY FERMIONS

Within a Kondo lattice, the strong hybridization between electrons localized in real space (r-space) and those delocalized in momentum-space (k-space) generates exotic electronic states called ‘heavy fermions’. In URu_2Si_2 we used spectroscopic imaging scanning tunneling microscopy (SI-STM) to image the evolution of URu_2Si_2 electronic structure simultaneously in r-space and k-space. Heavy-quasiparticle interference imaging within this gap reveals its cause as the rapid splitting below To of a light k-space band into two new heavy fermion bands. This was the first direct visualization of a Kondo-screening many-body state in magnetic lattice and the first use of heavy quasiparticle interference to determine a heavy fermion band structure (both above and below EF). This combined capability to simultaneously visualize the r-space Fano lattice and the k-space heavy fermion structure opens a completely new experimental window onto the physics of multichannel Kondo lattices and heavy fermion physics, and has generated great interest worldwide.

VISUALIZING THE DESTRUCTION OF HEAVY FERMIONS

Replacing a magnetic atom by a spinless atom in a heavy fermion compound generates a quantum state often referred to as a ‘Kondo-hole’. No experimental imaging had been achieved of the atomic-scale electronic structure of a Kondo-hole, or of their destructive impact on the hybridization process between conduction and localized electrons that generates the heavy fermion state. We recently reported the first visualization of the electronic structure at Kondo-holes created by substituting spinless Thorium atoms for magnetic Uranium atoms in the heavy-fermion system URu_2Si_2. At each Thorium atom, an electronic bound state is observed. Moreover, surrounding each Thorium atom we find the unusual modulations of hybridization strength recently predicted to occur at Kondo-holes (Figgins J, Morr DK (2011) Phys Rev Lett 107:066401). Then, by introducing the ‘hybridization gapmap’ technique to heavy fermion studies, we discovered intense nanoscale heterogeneity of hybridization due to a combination of the randomness of Kondo-hole sites and the long-range nature of the hybridization oscillations. These observations provide new and direct insight into both the microscopic processes of heavy-fermion forming hybridization and the macroscopic effects of Kondo-hole doping. Long-standing theoretical predictions for the electronic structure of a Kondo-hole including the suppression of hybridization near the substitution-atom sites the disordered hybridization fluctuations generated by random Kondo-hole doping, that an impurity bound-state appears within hybridization gap and that hybridization oscillations exist are borne out directly by these experiments. This agreement between theory deductions from macroscopic experiments provides growing confidence in the ability to predict theoretically and to detect experimentally the atomic scale electronic structure and, perhaps more importantly, the consequent hybridization disorder generated by Kondo-holes. The combination of SI-STM techniques introduced here provides a powerful new approach for study of the r-space and k-space electronic structure of heavy fermion systems.

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

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Funding:	$535,000

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.

Experimental and Theoretical Investigations of Spin Transport in Semiconductors

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Funding:	$122,000

An important objective of semiconductor spintronics is to generate electron spin polarization, and to preserve it for a sufficiently long time for possible information processing. On one hand, spin-orbit coupling enables optical generation and manipulation of spin polarization. However, spin-orbit interactions can also lead to rapid loss of the spin lifetime.

Nanoscale Magnetic Materials: Synthesis, Advanced Characterization and Technique Development

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Funding: $2,405,000

(A) Novel magnetic materials and nanoscale structures are synthesized and studied with a powerful range of techniques. The systems include vapor-phase deposited thin films and multilayers, patterned nanoscale systems, epitaxial and amorphous materials, metastable alloys, complex oxides, and ferroelectric/multiferroic films that are relevant to spintronics and magnetics. Calorimetry yields electron, phonon, and magnon densities of states, as well as magnetic ordering temperatures. Advanced synchrotron-radiation techniques yield element-specific electronic and magnetic structures, with spatial resolutions from micron to sub-nanometer scale, as well as time resolution to the picosecond scale. The methods include resonant soft x-ray scattering, soft x-ray microscopy, and high resolution spectroscopies (core- and valence photoelectron, x-ray absorption, x-ray emission and inelastic scattering), in some cases excited by standing waves. (B) Supports part (A) by providing soft x-ray nanoscale imaging of magnetic materials at the ALS XM-1 full field microscope, currently at routine spatial resolutions of 20 nm, but recently achieving a world record of12 nm, and improvement to 10 nm in the near future. Soft x-ray multilayer mirrors synthesized in this program are also key to the standing-wave studies in part (A).

The Magnetic Materials program additionally received at least half of the research effort of two postdoctoral fellows and three graduate students who were supported by outside sources (fellowship, TAship, etc).

Novel sp2-Bonded Materials and Related Nanostructures

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Funding: $1,085,000

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

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

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.

The Novel sp2-bonded Materials and Related Nanostructures program additionally received at least half of the research effort of two postdoctoral fellows and four graduate students who were supported by outside sources (fellowship, TAship, etc).

Quantum Materials

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Students:	6 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,433,000

Quantum physics provides the theoretical basis for our understanding of the electronic properties of all materials. However, there exists a fascinating sub-class of condensed matter systems, now widely known as “quantum materials,” in which quantum mechanics plays an especially profound role in determining the nature of macroscopic order parameters and the phase-transitions between them. In some cases, such as superconductors, this occurs because the order parameter is explicitly a quantum mechanical object. In many other such systems, quantum effects dominate the physics because of the interplay between competing order, frustration, strong interactions, and low-dimensionality. These systems display a marvelously rich and diverse range of physical phenomena. Transition metal oxides, e.g., manganites, cuprates, ruthenates and cobaltates, are systems whose interacting charge, spin, orbital, and lattice degrees of freedom exemplify the diversity of quantum materials.

Investigations of Electron Correlation in Complex Systems

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Funding:	$600,000

Electron correlation, the electron-electron interactions outside of simple one-electron models, is the key to resolving outstanding issues concerning the electronic structure of complex materials. These complex materials have intricate physical structures and/or multiple phases with unique electronic-structure properties. We will use cutting-edge techniques such as Resonant Inverse Photoelectron Spectroscopy (RIPES) and Fano Spectroscopy, a sophisticated variant of Photoelectron Spectroscopy (PES), and related techniques to determine the valence electronic structure of complex materials. In the past, these complex materials have included a broad range of materials. However, now we propose to focus solely on actinide materials, an area of world-class science and an issue at the core of the DOE Office of Science and Office of Basic Energy Research. Support measurements upon Rare Earth surrogate systems will be performed at the Advanced Light Source and the Advanced Photon Source. Highly radioactive samples will be interrogated with our unique capabilities at Lawrence Livermore National Laboratory. We will solve the Pu electronic structure problem, a goal of tremendous scientific and technological importance to DOE and the USA. We will provide experimental benchmarking for the new theories of Pu and actinide 5f electronic structure, leading to the resolution of a problem that has remained unsolved for the last 60 years, the nature of the 5f electron. A proper modeling of Pu electronic structure will, in turn, lead to an enhanced capability to predict the behavior of Pu over long periods of time, an issue of tremendous importance to environmental cleanup, radioactive waste storage and national nuclear security.

Quantum Electronic Phenomena and Structures

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Funding:	$140,000

Our goal in this project, which is part of a larger effort led by Sandia National Laboratories, is to understand the behavior of quantum-based nanophotonic and nanoelectronic structures through the use of ultrafast optical techniques, which allow us to separate their inherent complex many-body interactions in the time domain. We have primarily focused on using our advanced ultrafast optical capabilities to characterize carrier dynamics in semiconductor nanowires (NWs) as a function of various experimental and fabrication parameters, with the goal of elucidating novel phenomena in these quasi-one-dimensional systems. Recently, we have extended our previous pump-probe measurements of ultrafast dynamics in ensembles of GaN NWs to the single NW level, in order to remove the inhomogeneous broadening inherent to ensemble measurements. This was a significant challenge that required us to design and fabricate appropriate single NW samples and optimize the signal-to-noise ratio of our laser system for these challenging experiments. We have recently overcome these obstacles, allowing us to perform the first femtosecond optical pump-probe measurements on individual III-V NWs. Our measurements clearly reveal a dependence of carrier dynamics in single GaN NWs on both the polarization and the position of the focused pump and probe spots on the NW, which was not observable in measurements on NW ensembles. Future ultrafast optical experiments on single nanowires may also enable us to temporally and spatially resolve carrier transport in these quasi-one-dimensional (1D) systems on a sub-100 femtosecond time scale and sub-micron length scale, which will give substantial insight on their unique properties.

Science of 100 Tesla

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$835,000

This project utilizes the Multi-Shot Magnet (100TMSM) for fundamental science in condensed-matter physics systems. Designed to achieve 100T nondestructively, the magnet is presently fully operational to fields of 95T for 10 ms-duration pulses. Having reached a record breaking field of 97.4 T in 2011, it is currently the only capability in the world delivering magnetic fields for experimental science in excess of 90 T. Magnetic fields of such intensity are essential for tackling scientific questions that cannot be answered using the magnetic fields available at other laboratories. Such fields provide a non-invasive, reversible probe that couples directly to the spin and orbital degrees of freedom of electrons in solids, producing very 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, which are as yet poorly understood. In addition, high magnetic fields provide a tunable magnetic length scale (l = (25.7/B1/2) nm) that parameterizes the spatial extent of the wavefunctions of band electrons. Scientific areas benefiting from the increased energy scale and collapsed length scales include quantum magnetism, nanophysics, strongly correlated electron systems and the electronic structure of high temperature superconductors.

Towards a Universal Description of Vortex Matter in Superconductors

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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$605,000

Vortex physics became a major field in condensed matter and statistical physics since the discovery of the oxide HTS. Although the rich HTS vortex phenomenology arises from the large influence of the thermal fluctuations, there is no hard boundary between HTS and LTS, thus a comprehensive vortex matter description should be universal. However, interactions of vortices with material defects, which produce pinning, have been considered too complex and material dependent to be described in a general framework. In this project we are challenging this concept. Taking a fundamental science approach, we propose to develop a description of vortex matter in the presence of inhomogeneities, including flux pinning and creep phenomena, valid for all superconductors. By comparing and contrasting systems with vastly different properties under a broad spectrum of conditions including extreme ones, and by improving theoretical models, we intend to establish a general picture that cannot be obtained by studying individual systems. This will drastically enhance our capability for predicting, controlling and designing the behavior of vortex matter. The relevance of this study goes beyond existing materials, as yet-to-be-discovered superconductors will share most of the vortex physics explored here. We at LANL have a unique combination of expertise and facilities to perform this research.

Electronic and Optical Process in Novel Semiconductors for Energy Applications

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Funding:	$498,000

Advanced energy technologies require high-performance materials, which in photovoltaics translates to new semiconductor materials to efficiently absorb sunlight, and in solid-state lighting(SSL), to new semiconductor materials for direct conversion of electricity to white light. A goal of this project is the realization of semiconductor materials 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 green emitters for SSL, via technologies based on GaAs substrates. A key to transcending the present limitations is the understanding and control of fundamental electronic and optical processes in semiconductors, which is another goal of this project. Towards this, this project will focus on understanding the phenomena of spontaneous ordering in high bandgap lattice-mismatched GaxIn1-xP, and abnormal electronic structure and properties of isoelectronic dopants 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 semiconductor material with novel, useful properties.

Correlated and Complex Materials

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

The physics of correlated and complex materials is addressed using the combination of materials synthesis, compositional tuning, and crystal growth. The overarching theme is the discovery and investigation of novel cooperative phenomena and new forms of order in complex transition metal oxides, pnictides and Zintl phases. Phenomena such as charge and orbital ordering, coupling of magnetism and ferroelectricity, unconventional superconductivity, vortex pinning and dynamics, low carrier density ferromagnetism, 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 condensed matter 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.

Emergent Behavior in Low-Dimensional Systems

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Funding: $738,000

The goal of the Emergent Phenomena in Reduced Dimensionality project is to explore and exploit emergent phenomena in materials through reduced dimensionality at or near nanometer scales where changes in physical properties are anticipated due to confinement effects caused by quantum interactions or resulting from surface or interface effects. Materials receiving the greatest attention are those with novel magnetic, electronic, and transport properties. These materials include strongly correlated electronic systems such as transition-metal oxides (TMOs) where the complexity arises from nonlinear correlations between spin, charge, and lattice structure, self-organized magnetic nanostructure assemblies with novel interactions, and surface-based low-dimensional correlated electronic systems. The signature of this program is a unique experimental approach with a combination of both in-situ material growth and characterization and ex-situ novel device design and characterization. The experimental effort is closely coupled with theoretical modeling and analysis which provides both stimulus for new theoretical work and guidance for making prudent experimental choices. Our effort to connect the world of nanophysics with complexity and emergent phenomena in artificially structured materials offers a novel and necessary method to elucidate the most fundamental organizing principles of matter, which we intend to lead to tunable emergence in complex materials that will create a new generation of electronics having lower production cost, offer new functionalities and require less energy for operation.

Epitaxial Complex Oxides; Growth Mechanisms and Cooperative Phenomena

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Funding: $1,341,000

This program seeks a fundamental understanding of the factors that affect novel properties emerging at epitaxial interfaces between dissimilar complex-oxide materials. Specifically, we ask:

(1) How can interfacial properties be controlled and tuned by the appropriate choice of synthesis parameters and materials choices?

(2) How are electronic, magnetic, structural, and chemical reconstruction interrelated?

(3) How do interfaces interact to yield macroscopic properties?

(4) How do spatial constraints influence how a system responds to interfacial effects?

The synthesis of perovskite heterostructures is controlled at the atomic scale in advanced pulsed-laser deposition techniques using electron and x-ray scattering methods for in-situ diagnostics. A broad range of macroscopic measurements (magnetization, ferroelectricity, transport, optical properties, neutron diffraction, etc.) is combined with spatially-resolved methods (electron microscopy, atom probe tomography, neutron reflectometry, scanning probe microscopy and spectroscopy, etc.) to yield a complete picture of interfacial effects. Specific emphasis is placed on electronic transport both along and across the interfaces or in patterned wires, the emergence of electron gases and magnetization at interfaces between insulating materials, and the coupling between different order parameters. The anticipated impact of this work is an ability to create artificial materials with predetermined macroscopic properties by the deliberate stacking of epitaxial interfaces.

Quantum Tuning of Chemical Reactivity for Storage and Generation of Hydrogen Fuels

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Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$450,000

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.

Quantum Electronic Phenomena & Structures

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Students:	3 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding:	$1,190,000

This project contains two topical thrusts that address the issues of what novel types of quantum collective behaviors can emerge from nanostructures and how well this behavior can be controlled and manipulated. During the last FY, we have obtained many exciting results in exploring quantum electronic and optical properties in MBE/CVD grown and/or lithographically patterned nanoelectronic structures. We have highlighted a few of the achievements as follows:

(1) Impact of disorder on the 5/2 non-Abelian fractional quantum Hall (FQH) state. Recently, we examined how the nature of disorder affects the 5/2 energy gap and, thus, the stability of this state. We compared the gap data obtained in two types of samples: symmetrically modulation doped quantum-well (MDQW) samples and undoped heterojunction insulated gate field-effect transistors (HIGFETs).In MDQW samples, where long-range Coulombic disorder dominates, the energy gap drops quickly with decreasing mobility (or increasing disorder). On the other hand, in HIGFET samples, where the short-range neutral disorder dominates, the 5/2 energy gap shows only a weak mobility dependence. Our results clearly demonstrate that the two types of disorder play very different roles in affecting the stability of the 5/2 state.

(2) Re-entrant Negative Coulomb Drag in a 1D Quantum Circuit. Coulomb drag measurements were carried out between tunable vertically-coupled quantum wires. The Coulomb drag signal is mapped out versus the number of subbands occupied in each wire, and regions of both positive and negative drag are observed. Negative Coulomb drag signals are measured in two regimes: one at low electronic density when the drag wire is close to or beyond depletion and one at a higher electronic density when the drag wire has one or more single 1D subbands occupied. This is the first observation of a negative one-dimensional Coulomb drag signal in wires with a 1D subband occupancy greater than, or equal to one. We proposed the re-entrant negative drag signal in terms of localization, electron-hole asymmetry and band structure.

(3) Spatial Distribution of Defect Luminescence on GaN Nanowires. The spatial distribution of defect and band-edge luminescence of GaN nanowires was studied using spatially-resolved cathodoluminescence (CL) imaging and spectroscopy. Defect-related yellow luminescence was revealed to be primarily surface-related, possibly due to the diffusion of mobile point defects during growth. Mitigation of these surface defects will be the key to controlling the nanowire electronic properties via interface engineering.

In the following, we list several research projects that we plan for the next FY:

(1) Spin polarization of the fractional quantum Hall states in the first excited Landau level. Answers to the question of the spin polarization of the FQH states in this Landau level will help us to better understand the nature of these FQH states, in particular the 5/2 and 12/5 states, which are believed to be of non-Abelian and have potential applications in fault-tolerant topological quantum computation. We plan to systematically study the spin polarization utilizing the tilted magnetic field technique in ultra-high mobility two-dimensional electron systems.

(2) Double Quantum Wires. With the goal of studying 1D correlation physics we will use the new samples to measure 1D-2D tunneling, 1D-1D tunneling for a single subband and Coulomb drag between 1D wires. These effects should depend on the nature of the 1D ground state, and provide a useful tool to access Luttinger liquid effects. We will also develop a high frequency (~GHz) reflectometry technique for quantum computing measurements.

(3) Growth and Electronic Properties of Nanowires. We will focus on growth and characterization of core-shell nanowires, primarily Al(Ga)N/GaN and patterned InGaAs/GaAs nanowires, in order to continue our study of interface manipulation and engineering of nanowires, and the resulting effects on their electrical and optical properties. These core-shell nanowires will allow us to examine the novel structure and physics of 1D and 2D electron and hole gases that may be formed at the heterointerfaces in free-standing semiconductor nanowires, as predicted by our recent theoretical work.

Atomic Engineering Oxide Heterostructures: Materials by Design

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

The overarching science and technology goals of this research are to use techniques we have developed for atomic-scale synthesis of complex oxide heterostructures to address the Grand Challanges for basic energy sciences. The issues we investigate are central to the challenge of “how do we atomically design and perfect revolutionary new forms of matter with tailored properties” and are also important to the challenges of controlling processes at the electron level, in understanding and creating emergent phenomena, and in mastering energy and information on the nanoscale. X-ray spectroscopy, microscopy, and holography are used to examine the interface electronic structure and the lateral nanoscale static and dynamic order in magnetic oxides. Magnetotransport and scanning SQUID susceptometry are used to study artificial 2D superconducting oxide semiconductors, towards the development of the mesoscopic physics of d-electron systems. Theory and modeling are used to develop a deeper understanding of the data and motivate new experiments. The pursuit of all of these activities in thin film form naturally provides a basic platform for advanced technology development.

The overarching institutional goal of this newly launched project is to develop a world leading program on the atomic engineering of oxide materials which is fully integrated with the SIMES and SLAC community, both immediately and in the longer term development of team efforts. This will allow us to fully capitalize on the unique synergies arising from embedding this thin film effort within the existing strengths in single crystal synthesis and various advanced materials characterization and investigation capabilities. In particular, the current emphasis at SIMES on emergent and quantum phenomena in bulk materials and their surface properties leaves open space for developing novel phenomena at heterointerfaces, and connecting these fundamental studies to structures relevant for device applications. This project provides a bridge across this space, which together with the existing expertise in other projects will create a uniquely deep and broad center of excellence in the science and technology of complex oxides. This integrated structure will facilitate the long-term design of materials scientifically matched with the future facilities coming online, such as the new angle-resolved photoemission spectroscopy (ARPES) beamline at SSRL and new capabilities at both LCLS and LCLS-II.

Spin Physics	
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Funding:	$415,000

The Spin Physics program consists of two closely related subtasks. The first subtask of Orenstein and Zhang investigates spin transport in semiconductors and topological insulators. The second subtask of Goldhaber-Gordon and Manoharan directly measures and manipulates low-dimensional spin, isospin, and electron correlations using scanning probes (scanning tunneling microscopy and spectroscopy [STM/STS], a new tool termed "Virtual STM," and Scanning Gate Microscopy) via the precise control of nanoscale geometry through nanofabrication and nanoassembly.

Materials Chemistry

Institutions Receiving Grants

Investigations of Surface Structural, Dynamical and Magnetic Properties of Systems Exhibiting Multiferroicity, Magnetoelectricity, Thermoelectricity…	
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Funding:	$145,000

Our research is carried out with the aid of many experimental techniques of scattering monoenergetic (monochromatic) atomic helium (He) beams, at thermal energies, from surfaces. The probe is the surface equivalent of thermal neutron scattering from the bulk of condensed matter systems. We also employ computational techniques such as lattice dynamics, Monte-Carlo and molecular dynamics to analyze and interpret the experimental data.

Elastic and inelastic scattering of ground state (spin zero) He beams are used to study surface geometric (atomic) structures and surface dynamics (phonons), respectively. Elastic and inelastic scattering of metastable state (spin 1 triplet 23S) He beams are used to study the surface magnetic (antiferromagnetic, helical, spiral, etc.) structure and the corresponding spin dynamics, respectively. The novel technique of metastable helium atom scattering was pioneered by our surface physics group (SPG) at BU in the 1990s.

Our current research is focused mainly on two novel classes of materials:

(1) Magnetoelectric Multiferroics. Multiferroics have become one of the hottest topics of condensed matter physics and materials science in recent years. They are multifunctional materials in which two or more types of spontaneous fundamental ferroicities, namely, ferroelectricity, ferromagnetism ferroelasticity and ferrotoroidicity, may coexist. From a fundamental physics perspective, they present a fascinating laboratory to explore the microscopic mechanisms responsible for the coexistence. Compounds with only simultaneous magnetic and electric ordering are referred to as magnetoelectric multiferroics. Of particular interest in such materials is the existence of a cross-coupling between the magnetic and electric orders, a mechanism that has been long known as magnetoelectric coupling.The concurrent presence of these two order parameters in these materials engenders novel physical phenomena which can be of great technological potential, and offers possibilities for new device functions. Significantly, multiferroics could lead to a new generation of memory devices that can be electrically written and magnetically read.

(2) Strong Topological Insulators. A topological state is a new state of matter that is insensitive to details of the system's atomic structure and spatial symmetry. In the strong topological insulators an energy gap arises from spin-orbit interactions. The topological constraints associated with these systems give rise to a robust and exotic metallic surface that is protected by the constraints, namely, time-reversal invariance. The exotic metallic states are manifest as massless Dirac fermion quasiparticles with a linear conical energy-versus-momentum dispersion; they behave like photons but with a speed 300 to 600 times slower. The scenario of massless electronic quasi-particles interacting with the surface lattice comprised of massive ions is precisely the motivating factor for studying these systems. We are familiar with massless Dirac fermions in high-energy particle physics, namely, neutrinos; but neutrinos do not interact strongly with any kind of matter. Recent studies of their surface phonon dispersions, reveal an intricate signature of these interactions manifest as a V-shaped strong Kohn anomaly at a wave-vector of twice the magnitude of the quasiparticles Fermi wave-vector kF.

Quantum Dot and Quantum Wire Solids

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Funding:	$165,000

Our program involves the application of our high precision, nano-manufacturing approaches, developed in earlier years, towards addressing fundamental problems in solid state systems, with a particular attention to energy conversion and energy-efficient technologies (thermoelectrics, photovoltaics, and superconductors, and associated surface science). Our approach is to explore the fundamental physical limits of materials properties through nanostructured design and architecture, and to pay particular attention to the role that surface chemistry plays in determining such properties.

Two of our results from this past year were written up as BES weekly highlights for, I believe, the DOE Director. Those were our work on the phononic nanomesh thermoelectric materials, and our development of graphene templating for elucidating the structure of weakly adsorbed molecules (such as water) on surfaces under ambient conditions. One of our images of water, captured via graphene templating, appeared as the back cover of *Physics Today* in January 2011.

We have published nine DOE-supported papers over the past year in journals such as *Science, Nature Nanotech, J Am Chem Soc, and Nanoletters*. Our work was also featured in *C&E News* as their Science Highlight of the Week.

The graphene templating technique (*Science,* 2010) was initially utilized to determine the structure of water adsorbed onto the hydrophilic surface of mica under ambient conditions. We found that, at 40% relative humidity (RH), water adsorbed as atomically flat, faceted islands, each 3.7 Å high, implying that these islands were a single unit-cell-thick layer of ice. At higher RH, the ice is a continuous single layer, and then a second unit-cell-thick layer begins to grow. Before that layer is complete (at very high RH), the water adsorbs as liquid droplets. We also investigated the structure of two model organic adsorbates - tetrahydrofuran, and cyclohexane, also on hydrophilic mica (*JACS,* 2011). Like water, the THF and cyclohexane initially adsorb as crystalline islands, and we were able to assign crystal structures to those adlayers. There is a striking similarity between our observations of these adsorbate growth processes, and well-studied heteroepitaxial growth mechanisms that are observed in the growth of solid thin films (e.g., Frank-van der Merwe growth). Second, the fact that water, THF, and cyclohexane all adsorb as molecularly-thin, crystalline adlayers very likely has implications for how adsorbed molecules influence surface frictional forces. More recently, we have studied water on hydrophobic surfaces (graphite, H/Si(111), and functionalized mica) and we have been able to directly address the long standing puzzle of why hydrophobic surfaces, which should not have water adsorbed based upon bulk thermodynamic considerations, can actually have more adsorbed water than hydrophilic surfaces. Again, this has strong implications for frictional forces.

We have also investigated nano-architectural approaches towards controlling thermal conductivity independent of electrical conductivity is candidate thermoelectric materials (*Nature Nanotech,* 2010). We have found that it is possible to retain bulk-like electrical properties in nanomesh-structured single crystal Si films, while dropping the thermal conductivity to near the amorphous limit. We have continued to explore this area, and related phenomena associated with photovoltaic devices, since that publication.

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

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Funding: $170,000

Our work supported by DOE/BES has as its major objective the study of the reactions of main group compounds with important small molecules, such as hydrogen, olefins, nitrogen, and carbon monoxide, with a view to understanding the mechanism of such reactions, and ultimately developing new catalytic systems. The major focus of our work during fiscal year 2011 has concerned the activation of C-H bonds of various hydrocarbons under ambient conditions by two different types of heavier group 14 element compounds - the dimetallynes $ArM\equiv MAr$ (Ar = bulky terphenyl ligand; M = Ge or Sn) and metalylene $:MR_2$. This has led us to undertake extensive studies of the reactions of the compounds with cyclic and non-cyclic olefins to determine the mechanism of C-H activation. We have also undertaken parallel studies for the reactions of group 13 element multiple bonded species with the olefins. In addition, we are investigating the reactions of diarylgermylenes $GeAr_2$ with isonitriles. This is exemplified by the reaction of the diarylgermylene $;Ge(Ar^{Me_6})_2$ ($Ar^{Me_6} = C_6H_3\text{-}2,6(C_6H_2\text{-}2,4,6\text{-}Me_3)_2$) with ($CNBu^t$) which becomes C-H activated at room temperature to release 2-propene and form the hydrocyanide $(Ar^{Me_6})_2Ge(CN)H$ in virtually quantitative yield. We have characterized the products spectroscopically and by X-ray crystallography and we have determined the mechanism of the reaction by Vait Hoff and computational methods. Also, we have synthesized and characterized a new class of germanium and tin ethers of formula $O(MAr)_2$ (M = Ge, Sn; Ar = terphenyl) and the diradicals of formula $ArM(\mu\text{-}O)_2MAr$, which have been shown to have very high reactivity. Other work involved the investigation of the reactions of ammonia, organoamines, hydrazines, and phosphine with the dimetallynes and metalylenes. All these molecules react readily under ambient conditions. The hydrazine derivatives have been found to eliminate diimines under moderate heating with formation of the amido derivatives. We have summarized our recent work on the reactions of multiple and unsaturated bonded main group compounds with hydrogen, ammonia, olefins and related molecules in an Accounts of Chemical Research article. In addition, we have published four papers that have detailed our preliminary results in these areas.

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

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Funding: $162,000

The emphasis of our research is to develop sufficient fundamental understanding to allow the controlled preparation of nano-structuring 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 (LD-FTMS)) with modern surface imaging experiments (electron microscopy, and variable temperature ultra high vacuum scanning tunneling microscopy (STM)). These experiments are combined with conventional methods of UHV surface science (High Resolution Electron Energy Loss Vibrational Spectroscopy (HREELS), Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS)). 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 will be 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 such as LD-FTMS.

We will use a combination of STM and SEM to study the growth of mesoscopically ordered nanometer sized metal structures on well defined substrates such as highly ordered pyrolytic graphite (HOPG). We will continue to develop methods (e.g., photochemical deposition) to decorate nanometer scale metal oxide structures with transition metal nanoparticles.

Low-Density and High Porosity Hydrogen Storage Materials Built from Ultra-Light Elements

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Funding:	$252,000

This project seeks to develop innovative synthetic methodologies for the creation of advanced porous materials with optimized framework compositions and pore architecture to maximize gas sorption properties. The project integrates synthetic exploration, structural and topological analysis, with extensive studies on sorptive properties of various gases such as nitrogen, hydrogen, carbon dioxide, and methane to identify compositional and structural features required for enhanced performance of such materials.

One synthetic strategy is the development of low-density porous materials for increased gravimetric gas uptake capacity by employing lightweight elements such as Li, B, and Mg. The PI's group has developed two large families of Li-based porous materials. One family, called Lithium Imidazolate Frameworks, is based on the combined use of two types of charge-complementary ligands, and another family is based on the lithium-phenolate cubane clusters with either covalently-linked or hydrogen-bond-linked porous frameworks. Significant progress has also been made with magnesium-based porous materials, for example, through the syntheses of a highly symmetrical chiral magnesium-based crystalline porous framework with one-dimensional cylindrical nanotubular channels and the first example of porous frameworks constructed with magnesium trimeric clusters.

The second strategy that can be employed either independently or in conjunction with the strategy above is to enhance the binding affinity between the framework atoms and gas molecules by introducing functional framework sites. This can be achieved by developing novel materials with either uncoordinated Lewis acid sites (also called open metal sites) or uncoordinated Lewis base sites (called open donor sites here). Specifically, the PI's group is targeting functional groups such as aromatic -N(H)- donors found in metal azolate frameworks. To increase the percentage of open donor sites, ligands containing multiple triazole and tetrazole groups (i.e., polytriazole or polytetrazole) are of particular interest, because these ligands can achieve a high connectivity even if they only use one N-donor site (per triazole or tetrazole group) for bonding with metals, which makes it possible to achieve the highest percentage of open donor sites (67% for a triazole, and 75% for a tetrazole). Alternatively, heterocyclic ligands such as imidazoles, triazoles, and tetrazoles can be used in combination with carboxylates. One material developed with this approach has exceptionally high gas uptake properties, for example, with an uptake of 115.6 cm^3/g (5.2 mmol/g) carbon dioxide at 273 K and 1 atm.

In addition to the above two strategies focused on the framework compositional and localized structural features, this DOE project also targets the development of the optimum pore architectures for enhanced gas sorption. To maximize the pore space utilization, we are currently pursuing a unique synthetic paradigm which is based on the delicate pore space partition through nested pore architecture by using complementary coordination properties of multitopic ligands. One practical consideration in pursuing such nested assemblies is the exquisite control that such architectures might offer in terms of partition of the pore space and pore size for optimum fit with adsorbate molecules. The successful development of this family of nested materials would require the conceptual development of a generalized mechanism for establishing the radial inter-cage connectivity and for establishing the inter-cage communication so that the initial formation of a cage can dictate the growth of either the inner or outer cage based on the structural feature of the initially formed cage. A significant progress has been made in this regard during the past year, and the rapid progress is currently being made towards the development of such unprecedented pore architecture.

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

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Funding:	$242,000

The goal of this project is to synthesize a new class of organic molecular metals and superconductors based on neutral carbon-based radicals. While most organic conductors are based on charge transfer salts, the elemental metals such as sodium and copper are based on the crystallization of atomic radicals in which the unpaired electrons ionize in the solid state to produce a free electron gas.

During FY 2011 year we focused on the synthesis and crystallization of substituted phenalenyl-based neutral radical with low disproportionation potential and we made significant progress in the synthesis of new phenalenyl derivatives. In the current funding period we have discovered a synthetic route that allows the introduction of sulfur and selenium substituents into the phenalenyl ring system. We have already synthesized, crystallized and characterized some thioalkyl substituted phenalenyl radicals. We have extended our synthetic effort on the alkyl thio substitution and we have now isolated some new thio- and seleno-bridged 9-hydroxy phenalenones and synthesized a number of boron salts containing thio and seleno bridged phenalenones which show very promising results with respect to the disproportionation potential. Our current focus is on the crystallization of these neutral radicals. We continue to work on the alkoxy-substituted phenalenyl boron radicals.

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

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Funding:	$221,000

This continuing proposal in the area of Materials Chemistry describes a successful, systematic approach to the postsynthetic modification (PSM) of metal- organic framework (MOF) materials. To further advance the utility of MOFs in the area of gas storage and other applications (particularly in energy applications), the ability to chemically modify these structures in a predictable and reliable fashion is essential. Realization of this goal will allow for the preparation of functionalized MOFs, which will have unparalleled properties, such as controlled framework flexibility and highly unsaturated metal sites. This research program will develop new methods to chemically modify MOFs. We will expand the scope of reactions that can be performed within MOFs by introducing new chemical 'handles' within the framework. Studies will focus on 1,4- benzenedicarboxylate (BDC) ligands, and extended analogues, possessing amino-, nitro-, or bromo-substituents. Other substituents can also be used by application of a new method, termed postsynthetic deprotection (PSD). Ligands with these chemical handles will be assembled into a variety of known MOFs, including IRMOF, UMCM, MIL-53, and UiO-66 architectures.

Proposed studies will also focus on the development of systems that contain two or more, orthogonal chemical handles on a single ligand (e.g., a bromo- and amine- group). These ligands will be used to produce MOFs where more than one PSM reaction can be performed. Importantly, these bifunctional systems will allow for control over the relative orientation of newly introduced functional groups, a feat not yet achieved in PSM chemistry. Slightly more applied studies will focus specifically on using PSM (or PSD) to control the selectivity, energetics, and capacity of gas sorption in MOFs. Our published findings show that PSM can be used to control MOF flexibility ('breathing'), improve heats of binding (for H_2), and facilitate introduction of unsaturated metal centers. Better understanding and control over these features will be pursued in our ongoing investigations.

In summary, our research program will continue to advance the fundamental principles and applications of PSM. Our improved capacity to modify MOFs in this manner will be important for the synthesis of new materials, altering the physical properties of these materials, and ultimately the use of these materials in advanced energy applications.

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

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Wudl, Fred, CALIFORNIA, UNIVERSITY OF SANTA BARBARA
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Funding: $600,000

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 temperaturedependent 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

The aims of this recently renewed proposal is to apply recently developed experimental techniques, and develop new ones, to make 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), conducted under conditions of “engineering interest.” The project involves modifications or new attachments to the Surface Forces Apparatus (SFA) allowing for simultaneous measurements of forces and other material properties such as the nano- and micro-structures of the surfaces and thin films, and how these change with time during an interaction.

In 2011 we developed and started to use new experimental techniques to create patterned surfaces and investigated the adhesion and (anisotropic and “3D”) friction of randomly rough, patterned and nanoparticle-coated surfaces, and correlated wear damage with tribological characteristics such as the friction coefficient. We also characterized “shudder” (resonance friction) and wear in model machine and automotive systems under extreme conditions. New results have also been obtained on the electrochemical forces between rough surfaces and fundamental studies on the phenomenon of corrosion (electrochemical) dissolution and damage.

Our experimental work is proceeding in collaborations with other top experimentalists and theoreticians/modelers worldwide.

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

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Funding: $128,000

Our work has three broad goals: (1) modification of surfaces on short length scales to alter the local symmetry and to create novel scientific phenomena involving liquid crystals, (2) investigation of liquid crystalline phenomena — both nanoscopic and macroscopic — arising from nanoscopically-controlled surface modification, and (3) development and enhancement of new device concepts that may be achieved by nanoscopic surface manipulation. Within these areas we examine issues such as wetting and dewetting effects on surface-induced order, the induction of surface chirality using achiral materials and the resulting physical phenomena that arise from the reduced symmetry, phase transitions and phase separation near regions of high director curvature, and topological defects. Much of our work has involved chirality transfer from chirally patterned substrates to the adjacent (and otherwise achiral) liquid crystal. We also have studied issues involving chirality transfer from chiral nanoparticles such as carbon nanotubes and the induction of molecular deracemization from macroscopic torsional strain. As a body, these investigations are designed to increase significantly our understanding of how liquid crystals behave when subjected to a reduced symmetry environment and how they may be manipulated on very small length scales.

Measuring the Importance of Valence to Chemistry of Nanocrystal Surfaces

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Funding: $150,000

Surface structure is central to the properties of colloidal semiconductor nanocrystals. Nonetheless, the valence of atoms on nanocrystal surfaces and its influence on the bonding and exchange of their ligands remains an essentially unexplored avenue of their chemistry. Current descriptions of semiconductor nanocrystal surfaces do not adequately distinguish between dative ligand interactions (L-type binding) and ligands that balance their charge with nonstoichiometric crystals (X-type binding). To address this problem we propose to study the relationship between nanocrystal stoichiometry and the exchange of both X- and L-type surface ligands using nuclear magnetic resonance spectroscopy. We aim to determine their thermodynamic binding constants and to study the mechanisms and kinetics of their exchange.

Powerful methods to exchange surfactant ligands will allow us to fabricate thin films of nanocrystals with an intact nonstoichiometric metal-ligand surface layer. We propose new methods to controllably deposit films of nanocrystals using layer-by-layer dipcoating and electrodeposition where the X-type organic surfactant ligands have been replaced with a halide ligand shell. With our techniques nanocrystal thin films can be deposited with a small internanocrystal separation and therefore enhanced electronic coupling. By maintaining the metal-halide surface layer within the film we will investigate its role in passivating electrical trap states. Fabrication of field effect transistor devices using these methods will allow us to relate the details of atomic surface structure with measurements of electrical transport. Such studies are a promising step toward optoelectronic devices with high carrier mobilities and low concentrations of charge trap states that are deposited from solution.

These studies are vital to the mission of the Department of Energy. To date, nanocrystal researchers have heavily relied on a L-type ligand model when describing nanocrystal surfaces. This model is implicit in numerous interpretations of experimental results, and has guided the design of ligand exchange reactions used to deposit thin films from solution and theoretical models. As a result clarifying the importance of X-type ligands to nanocrystal surface chemistry and its relationship to stoichiometry can have a dramatic influence on all avenues of nanocrystal research. By investigating X-type ligand exchange we stand to gain powerful methods to precisely tailor nanocrystal surfaces. In particular, these methods can preserve the role of excess surface metal ions in trap state passivation, and may offer cast improvements in nanocrystal thin film optoelectronic devices.

Development of Methods to Synthesize Nanoparticles of Ordered Intermetallic Compounds (Binary, Ternary, and Quaternary): Application to Fuel Cell Elec

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Funding:	$270,000

The adoption of fuel cell technologies, especially those based on polymer electrolyte membranes 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.

Only a few fuels can be directly used in polymer electrolyte fuel cells, namely hydrogen, formic acid, and ethanol. Anode catalysts do not yet exist that will fully oxidize other fuels. Further, when hydrogen is the fuel, the anode catalyst (usually platinum) can lose activity due to “poisoning” by impurities such as carbon monoxide and sulfur containing molecules. At the cathode, the reduction of oxygen is kinetically too slow. Platinum or platinum-cobalt alloys are currently the best catalysts for oxygen reduction, but large improvements (many orders of magnitude) in the reduction rates are needed in order to increase the efficiency of the fuel cell and lower catalyst loading.

However, new catalysts must be prepared in nanoparticle form. New and improved catalysts are expected to be binary, ternary or even quaternary ordered intermetallic compounds. Consequently, the research proposed here will explore, develop and understand the synthetic procedures that are needed to prepare such nanoparticles.

The synthetic method employed in this research is the reduction of solutions of appropriate metal precursors, mixed at the desired composition, by a suitable reducing agent. The resulting nanoparticle products of such reductions are very dependent on all the components involved (precursors, reducing agent, solvent, ligands, anions) as well as the temperature of reaction or subsequent heating after reduction. Methods of attaching the nanoparticles to a variety of conducting supports will be explored as well, since conducting supports are needed in fuel cell applications. A variety of tools will be used to characterize the structure, composition, surface properties and electrochemical activity of these nanoparticles. The goal is to understand the mechanistic details of reaction well enough to be able to design syntheses that will work for a broad range of potential compositions of catalysts that will be discovered by collaborators at Cornell, who are experts in combinatorial materials chemistry.

Potential Impact: If the research is successful, it will likely have a large impact in helping fuel cell technology reach the marketplace by making it more robust and affordable. The methods developed can be applied to other electrochemical technologies, such as supercapacitors and batteries, to gas phase catalyst systems, and to the preparation of a wide variety of nano-particle materials.

Low Temperature Synthesis of Carbide-derived-carbons from Binary and Ternary Carbides in the Si-Ti-C System: Experiments and Modeling

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Funding:	$150,000

Carbide-derived-carbon (CDC) is an evolving class of tunable nano-structured functional materials that show promise in many fields of application, such as energy and gas storage. Results from the previously funded period gave new insights into SiC-CDC and control of the carbon nanostructures as a function of sample pre-treatment and carbon formation conditions, such as gas pressure and temperature.

Recently, we investigated low-temperature CDC formation on nanosized TiC powder via chlorination. Here, we observed CDC formation at temperatures as low as 180°C. The resulting CDC nanostructures were highly disordered with a large fraction of pores smaller than 0.4 nm. Furthermore, low-temperature CDC materials are characterized by an extremely high reactivity shifting the onset of oxidation from > 400°C to approximately 200°C.

In this proposal, we outline our plans to expand our study from SiC alone to binary and ternary carbides of the Ti-Si-C system (i.e., TiC, SiC and Ti_3SiC_2). Our research will address CDC formation and structural evolution at temperatures below 400°C.

We chose the Ti-Si-C system for several reasons. First, carbides from this system were shown to yield reproducible, tunable CDC materials at higher temperatures. Considering the conformation transformation of the carbide into carbon, carbides with heavier metal ions yield extremely porous carbon, which is likely to cause delamination of CDC thin films. Also, the chosen carbides are widespread in their application and different high-quality carbide material (nanopowder, micropowder, whisker, single-crystals, thin films etc.) can be purchased from various suppliers. More importantly, the different bonding strength between the metal ions and carbon in these carbides allows us to investigate possible limitations of low-temperature CDC formation and strategies to overcome them. In case CDC formation is limited by the presence of a native oxide scale (silica on SiC), removal of that oxide will enable carbon formation. Parametric studies on sample pre-treatment will elucidate this aspect.

An important method for kinetic studies on CDC formation via low-T chlorination will be in-situ Raman spectroscopy. It will be the first time that this method will be applied as a tool to monitor structural CDC formation. With the high sensitivity of Raman spectroscopy for the structural characterization of carbon materials, this method was an important tool in the previously funded research and will continuously be accompanied with other analytical tools to characterize the structural (electron microscopy, IR-spectroscopy, XPS), mechanical (nanoindentation), and electrochemical (potentiostatic and galvanostatic studies) behavior along with the pore size distribution and bulk pore volume (gas adsorption measurements).

This project will address low-temperature chlorination as a new way to inexpensively produce highly reactive CDC material with high potential in the fields of gas and energy storage on a mass-production level once the basic principles and limitation of CDC formation are understood. Until now, the lack of systematic basic science studies greatly limits CDC applications.

Luminescence in Conjugated Molecular Materials Under Sub-Bandgap Excitations

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Light emission in semiconductors occurs when they are under optical and electrical excitation with energy larger than the bandgap energy. In some low-dimensional semiconductor heterostructure systems, this thermodynamic limit can be violated due to radiative Auger recombination (AR), a process in which the sub-bandgap energy released from a recombined electron-hole pair is transferred to a third particle leading to radiative band-to-band recombination. We have demonstrated that efficient electroluminescence in poly[2-methoxy-5-(2’-ethylhexyloxy)-1, phenylenevinylene] (MEH-PPV) polymer light-emitting devices (PLEDs) at drive voltages below its bandgap voltage could be observed when a ZnO nanoparticles (NPs) electron injection layer was inserted between the polymer and the aluminum electrode. Based on these data, we propose that the sub-bandgap turn-on in the MEH-PPV device is due to an Auger-assisted energy up-conversion process.

Based on our data, we study the sub-bandgap turn-on in MEH-PPV devices due to Auger-assisted energy up-conversion process. Specifically, we would like to determine whether the up-conversion process is due to charge accumulation at the polymer/NPs interface. This model requires that holes should be the dominant carriers in the polymer and the polymer/ZnO NCs heterojunction should be a type II alignment. In order to determine the mechanism of the up-conversion process, we will characterize devices fabricated using polymers with different carrier transporting properties to determine whether hole accumulation at the polymer/nanocrystals is required. Likewise, we will also use nanoparticles with different electronic structures to fabricate devices to determine how electron accumulation affects the up-conversion process. Finally, we will measure quantitatively the interface charge accumulation by electroabsorption and correlate the results with the up-conversion photoluminescence efficiency measurements under an applied electric field.

Guided Assembly of Anisotropic Micro-Structures Into Mesoscale Hierarchies

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Several different tasks have been elaborated during the last year.

MANUFACTURING ANISOTROPIC ECO-CAPSULES AND ITS ASSEMBLY

Preparation of cubic microcapsules with well-defined shape by LbL technique includes sodium chloride cubic cores that were coated by multiple depositions of alternate layers of poly(methacrylic acid) (PMMA) and poly(N-vinylpyrrolidone) (PVPON). A nonhazardous core release by water has been used. The overall thickness of these LbL shells with four bilayers is within 20 nm which is twice higher than for the LbL shells produced from the aqueous solutions.

Assembling of the cubic capsules dispersed in water, polar and non-polar solvents in contrast to the spherical capsules. The cubic capsules form the highly compacted 3D cubic arrays due to the face to face interactions and steric confinements in sharp contrast to the assembly built by the spherical capsules for which the hexagonal packing is generally favored. The assembled spherical microcapsules create a large number of openings while the cubic microcapsules build close, compact aggregates. Thus the porosity of the cubic assembly is mainly caused by the nano-porous shells which can be tuned by solvent composition.

FLUORESCENCE ENHANCEMENT OF POLY(P-PHENYLENEETHYNYLENE) FLUORESCENT POLYMER ON SILVER NANOCUBES COATED WITH DIFFERENT HYDROGEN-BONDED LAYER-BY-LAYER ASSEMBLED SHELLS

Nanocomposites consisting of a cubic silver (AgNC) nano-core, a hydrogen-bonded polyelectrolytes-spacer shell with controlled thickness and a poly(p-phenyleneethynylene) (PPE) was fabricated by utilizing LbL assembly of poly(vinyl pyrrolidone) and PMAA. Langmuir-Blodgett (LB) was used to assemble the cubic core-shell nanoparticles on the surface of a quartz glass for the investigation of the fluorescence enhancement of the PPE polymer by AgNC.

The surface plasmon resonance spectrum of the core-shell cubic nanoparticles in dry state and in the swollen state show two characteristic peaks at 470 nm and 670 nm that are attributed to silver cubes and their aggregates, respectively. The fluorescent intensity of PPE coated core-shell nanoparticles increases as the thickness of the separating shell increases. The optimum separation distance at which fluorescent intensity increased by 60 times in the swollen state and 30 times in the dry states was found to be 15 nm.

DEPENDENCE OF THE PHOTOPHYSICAL PROPERTIES OF POLY(PARAPHENYLENEETHYNYLENE) POLYMER ON CHAINS LENGTH: PURE POLYMER VERSUS HYBRID WITH SILVER NANOCUBE MONOLAYER

The photophysical properties of three poly(paraphenyleneethynylene) fluorescent polymers, varying in chain length, were studied as a function of (1) pure polymer surface compression after deposition from a LB trough onto a substrate and (2) deposition of a constant amount of polymer onto the surface of silver nanocube arrays of varying particle densities. The results are discussed in terms of the surface pressure and nanoparticle topography effects on conformation of the fluorescent polymer. A combined effect of conformational changes shifts the emission to higher energy (blue-shift) and plasmonic effects that result in enhancement of primary emission of the polymer (emission from the 0-0 and 1-0 transitions), thus narrowing the emission. There were a total of four papers published in 2011.

The Organic Chemistry of Conducting Polymers: From Molecular Wires to Photovoltaics

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We are examining the fundamental principles of conduction in one-dimensional systems, i.e., molecular “wires.” Interchain hopping and grain-boundary resistivity are limiting conductivity factors in highly conductive materials. A partial breakthrough to this limitation may be represented by the extraordinary progress in the use of graphene as an electronic material, although grain-boundary problems also exist for graphene. However, this two-dimensional material can be shaped, molded, and cut into appropriate feature sizes which both limit and control charge transport in such systems. We are examining the basic principles underlying charge transport (the “rules of the game”) in two-dimensional systems by using model systems which allow direct observation of such processes. We are studying the principles underlying charge transport in two- and quasi two-dimensional systems by using graphene “nanoribbons.” In addition we are completing studies on bulk-heterojunction (Grätzel) solar cells using organic blocking layers.

Controlling Magnetic and Ferroelectric Order Through Geometry: Synthesis, Ab Initio Theory, and Characterization of New Multi-Ferroic Fluoride Material

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Funding: $339,000

Transition-metal fluoride materials have been studied extensively attributable to their important magnetic, electric, multi-ferroic, and optical functionalities. Specifically, iron fluoride compounds have been investigated owing to their fascinating structural topologies and unusual physical properties. For example, ferric fluoride (FeF_3) is found in rhombohedral, hexagonal tungsten bronze, pyrochlore, and amorphous forms and has been shown to exhibit magnetic frustration. Interestingly, some mixed valent iron compounds also exhibit unusual magnetic properties as well as ferroelectricity. For example, $K_3Fe_5F_{15}$, which contains three Fe^{2+} ions and three Fe^{3+} ions, shows multi-ferroic behavior. Mixed valent and ordered Fe^{2+}/Fe^{3+} fluoride compounds are relatively rare, attributable to their synthetic preparation as well as the control of the oxidation states. We have developed a low temperature hydrothermal method using CF_3COOH, instead of $HF_{(aq)}$, that has enabled us to synthesize a variety of new mixed valent and ordered Fe^{2+}/Fe^{3+} fluoride compounds. We initially used this technique to synthesize the $BaMF_4$ family (M = Mg, Mn, Co, Ni, and Zn) (J. Am. Chem. Soc. 2010, 132, 17684). Surprisingly these materials had not been synthesized in the bulk, but only as crystals through the use of either $HF_{(g)}$ or $CF_{4(g)}$.

With respect to mixed valent fluoride materials, we have synthesized $RbFe_2F_6$ and $K_4Fe_3F_{12}$. Both compounds may be written more descriptively as $RbFe^{2+}Fe^{3+}F_6$ and $K_4Fe^{2+}Fe^{3+}{}_2F_{12}$, and both have Fe^{2+} and Fe^{3+} ordered throughout the crystal structure. The former exhibits a pyrochlore-related crystal structure with Kagome-type nets in two planes. Variable temperature neutron diffraction measurements indicated that is $RbFe^{2+}Fe^{3+}F_6$ anti-ferromagnetic (a Curie-Weiss temperature of -270K) as well as significant magnetic frustration, $\theta/T_N = 17$. Variable temperature neutron diffraction measurements did not reveal any structural transitions down to 4K. The magnetic structure was determined from the powder neutron data. Theoretical calculations were performed (GGA and GGA+U) and are consistent with an anti-ferromagnetic ground state. The paper on $RbFe^{2+}Fe^{3+}F_6$ is currently under in press at Chemical Sciences. With $K_4Fe^{2+}Fe^{3+}{}_2F_{12}$ neutron diffraction measurements are currently underway, but magnetic measurements indicate the material is also anti-ferromagnetic.

Enhanced Mixed Electronic-Ionic Conductors Through Cation Ordering

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Funding: $400,000

The work concerns multiple areas of Solid Oxide Fuel Cell (SOFC) cathodes related to their fundamental properties and catalytic ability.

(1) Thermodynamics of oxygen non-stoichiometry of the ordered perovksites $REBaCo_2O_{5+x}$ (Jacobson). The ordered perovksites have some of the best oxygen transport and surface exchange rates measured for mixed ionic and electronic conductors. We are experimentally determining the properties of selected compositions as a function of temperature and pO_2. An understanding of the oxygen non - stoichiometry is of underlying general importance. We have used sealed electro chemical cells to determine the oxygen non-stoichiometry of $PrBaCo_2O_{5+x}$ as a function of T and pO_2. Surprisingly the results indicate a first order phase transformation at the composition $PrBaCo_2O_{5.25}$. A defect model is being developed with Morgan to analyze the data. Measurements on $NdBaCo_2O_{5+x}$ are in progress.

(2) Neutron Diffraction studies of the structures and non-stoichiometry of $REBaCo_2O_{5+x}$ (Jacobson). In collaboration with McIntosh at Lehigh we have recently completed a series of high temperature neutron measurements at SNS on $PrBaCo_2O_{5+x}$ and $NdBaCo_2O_{5+x}$. The results complement the stoichiometry measurements and give structural details.

(3) La-Sr ordering in thin-film $La_{0.5}Sr_{0.5}CoO_{3-x}$ (LSC) (Morgan). In close collaboration with co-PI Jacobson we have used ab initio methods to determine how strain might alter anion defect formation and cation ordering and diffusion in strained thin-films of LSC. We demonstrated that strain could significantly enhance the anion vacancy content as well as increase cation mobility. Together these effects were used to explain the ordering of La and Sr in LSC thin-films observed by Jacobson and collaborators. This ordering had never before been observed and opens a new path to manipulating LSC performance through cation ordering.

(4) Descriptors for SOFC cathode activity (Morgan). We have used ab initio methods to find descriptors that can predict SOFC cathode performance. We show that area specific resistance (ASR) and oxygen exchange rates (k*) are correlated with ab initio calculated oxygen p-band centers and oxygen vacancy energies in mixed electronic-ionic conducting perovskites. This result represents 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. These results open the door to practical ab initio based design of SOFC cathodes.

(5) Local structure and oxygen transport mechanism in La_2NiO_4+d (Grey). For this project the local structure and oxygen transport mechanism of Ruddlesden-Popper type La_2NiO_4+d, a candidate as an intermediate temperature SOFC cathode material, is being investigated by using ^{17}O and ^{139}La NMR techniques at various temperatures. The study will be supported by first principles calculations using the CASTEP code. NMR methods will be used to investigate local structure and dynamics of the oxygen ions. Preliminary NMR results for the orthorhombic phase at ambient temperature show a sharp resonance at 532 ppm, which is assigned to the interstitial oxygen sites. The other oxygen sites are nearby paramagnetic Ni ions and their resonances are shifted out of the normal chemical shift range for ^{17}O; two different magnetic fields were required to resolve these oxygen environments.

Cathode Catalysis in Hydrogen/Oxygen Fuel Cells

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Funding:	$350,000

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), which is the electrochemical process that most fundamentally limits the technological utility of these environmentally benign energy conversion devices. It is therefore to the single greatest challenge limiting wide-spread implementation of hydrogen-oxygen fuel cells, that provide robust low cost cathodes that efficiently reduce dioxygen to water, that we address the work performed in this project.

Utilizing support from this project, we developed a new class of ORR catalyst, based on Cu dimers and multimers. These new materials exhibit ORR onsets at potentials higher than any other Cu-based material in neutral and basic environments and are inspired by the three-Cu active site in laccase which has the highest ORR onset potential of any material known. By directly coupling laccase to a Au electrode we showed that this three-Cu active site in laccase is especially competent for the ORR. We also used microfluidic methods to evaluate these catalysts in both the acidic and basic electrochemical environments. We have developed new XAS and microscopy based techniques with which to study the ORR, which provide insight into the ORR active site with unprecedented resolution. These techniques have helped us to develop insights into ORR reaction mechanisms on important electrocatalytic materials. In turn, these insights are providing directions to synthesize new ORR catalytic materials.

Programming Function via Soft Materials

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Funding:	$1,607,000

The overarching goal of our cluster 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.

Our approach to Programming Function via Soft Materials integrates three core research areas:

(1) Dynamic supracolloidal assemblies – created by controlling the equilibrium and nonequilibrium phase behavior, spatial organization, and connectivity of colloidal particles, clusters, and mixtures thereof through self, driven and chemically amplified assembly and disassembly pathways.

(2) Deterministic assembly of fluid and solid inks – to precisely pattern micro/nanostructured materials in the form of conductive pathways via omnidirectional printing and as solid "inks" composed of III-V heterojunctions via transfer printing.

(3) Functional architectures for light capture and utilization – in flexible "skin-like" motifs. Light collection and light emitting systems based on large microcell arrays represent new technologies that are uniquely enabled by our scalable approaches and fundamental understanding of function-encoded building block synthesis and assembly.

Charging and Polarization of Organic Semiconductors in Energy-Efficient Circuits and Energy Capture Models: Synthesis, Electronics, and Spectroscopy

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Funding:	$275,000

We are the first to demonstrate switching voltage tuning and improved gain by applying static charge to an organic transistor dielectric prior to depositing semiconductor and contacts. A high electric field is created via corona voltage, on the order of +/-10kV, and the grid voltage defines the total charge level in the dielectric. A charging time of about 10 minutes is enough to acquire uniform charge density over the dielectric material used. Atactic polystyrene was locally charged through patterned Cytop/photoresist, layer, leaving patterns of charges in the film. For n-channel transistors, N,N'-bis(2(pentafluorophenyl)ethyl)- 1,4,5,8-naphthalene tetracarboxylic acid diimide (5FPE-NTCDI) is sublimed. The same deposition technique is used for the p-channel transistors over the negatively charged regions, where 50nm of pentacene is deposited. For 5FPE-NTCDI OFETs, a change of -35V is observed in the threshold voltage on a +50V charged sample. There was no change in mobility, on/off ratio, or the subthreshold swing of the transistor, implying that no additional traps were created at the semiconductor/dielectric interface because of the stored charge. A similar effect on threshold voltage was observed in a pentacene transistor which was charged with -25V and showed a shift in threshold voltage of 10V. We also developed the first silicon-on-insulator (SOI) integration technique for organic field effect transistor (OFET) based circuits. We fabricated p- and n-type transistors, and proof of concept OFET-based complementary circuits, such as inverters and NAND-gates. Static charging determines the exact position of the inverter switching voltage.

We are beginning a multipronged effort to visualize the charge distributions and identify charged species in semiconductor-dielectric bilayers with embedded static charge and/or interfacial voltage.

Using Surface Kelvin Probe Microscopy (SKPM), we build on our pioneering result from the previous project period in which we imaged the voltage drop at an organic lateral pn junction. We can now visualize a voltage drop at an organic semiconductor-dielectric interface in a lateral geometry. We mimic as much of the organic transistor layout as possible in an accessible, sideways orientation. We use a sample with adjacent pentacene and polystyrene (PS) films. Before charging, the surface potential on the pentacene side can be raised above the PS side, while after the +200V charging, the surface potential on the PS side remains greater than the pentacene throughout, enabling the visualization of the potential differences that led to the threshold voltage shifts discussed above. Conversely, negative charging results in lowering the PS surface potential and the pentacene surface potential remains below the PS surface potential throughout. Also, lower absolute values of charging voltages result in lower surface potential differences between the PS and pentacene.

We are now extending our characterization techniques to include thermally stimulated discharge current, surface sum frequency generation, and Raman spectroscopy. Finally, we are performing finite element modeling of the charge distribution in the molecular semiconductor solids in response to applied and local fields.

Biaxiality in Thermotropic Bent-Core and Tetrapodic Nematic Liquid Crystals

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Funding:	$350,000

The focus of this project is the phenomena of biaxiality in the nematic and smectic liquid crystals (LCs). Liquid crystals are fluids, composed of anisotropic molecules, which possess some degree of orientational and/or positional order. Plank-like or bent-core molecules give rise to the possibility of forming optically biaxial nematic and smectic LC phases. The thermotropic biaxial nematic phase predicted more than 40 years ago remained elusive until its discovery in 2003 in bent-core mesogens by Kumar, et al. Five interdisciplinary researchers are investigating biaxiality in LCs using fluorescence confocal polarizing microscopy (FCPM), micro-Raman spectroscopy (MRS), synchrotron x-ray scattering, and dynamic light scattering. The objective of project includes the following:

SYNTHESIS OF NEW LC MATERIALS AND PHASE BEHAVIOR

The structure and the nature of LC phases and their dependence on molecular architecture are being studied exclusively in bent-core mesogens. One of the research groups is synthesizing unique bent-core molecules having 5- and 6-rings with different terminal and linkage groups, with different apex angles, and with a chiral center. New synthesis pathways to compounds with low temperature biaxial nematic phase and the previously predicted ferroelectric nematic phase are being devised.

PHASE DIAGRAMS AND CRITICAL BEHAVIOR

The topology of the phase diagrams is determined to test the predictions of current theories/simulations (e.g., existence of Landau point or a linear phase boundary between the isotropic and biaxial nematic phases). Quantitative studies of critical behavior at the transitions between the isotropic, two uniaxial nematic, biaxial nematic, and smectic phases in these (single component and mixtures) materials are planned in specific compounds. Experimental investigations of the various phase transitions will yield critical exponents associated with positional order correlations and uniaxial and biaxial nematic order parameters. These investigations will provide insights into the nature of these transitions and symmetry of the biaxial nematic and smectic phases, and will test the theoretical predictions.

BIAXIAL ORDER AND DEFECT TEXTURES

The biaxial order parameter, elastic constants, their temperature dependence, and the effect of biaxiality on elasticity and viscosities of LC phases will be determined using MRS and FCPM techniques. High-speed video imaging will be used to study static and dynamic topological defects in 3-D and the escape of one of the directors in the third dimension near 2- or 4-brush disclinations in the uniaxial and biaxial nematic phases.

The research will provide a sound understanding of the biaxial phenomena and test the validity of assumptions/concepts that form the foundation of the theoretical models and simulations, leading to our ability to tailor desired phase behavior and physical properties. Faster optical switching of biaxial nematics is expected to lead to disruptive new technologies for electro-optical and photonic devices. A number of graduate students and postdoctoral scholars will be mentored in advanced scientific research. A natural progression of this work is likely to lead to exotic materials such as ferroelectric nematic fluids.

Electronic and Ionic Conductors from Ordered Microporous Materials

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Funding:	$150,000

This project aims to develop rational pathways towards the synthesis of ordered microporous materials with tunable electron and ion transport properties. Research will focus on developing new synthetic routes towards the isolation of electronically active, highly porous metal-organic frameworks (MOFs). By combining the synthesis of electronically active bridging ligands with rigorous topological design principles, a cluster-directed approach towards porous and conductive MOFs will be developed. A complementary approach involving a novel inorganic charge-transport formalism will also be explored. Finally, topochemical ion metathesis reactions are proposed for the synthesis of MOF-based Li^+ and Na^+ ion conductors. The electronically active microporous materials resulting from this research will display unique, tunable multifunctional properties with a potential impact in electrical energy storage, electrocatalysis, and ion conductors, among others.

Crystallization-Driven Assembly of Conjugated-Polymer-Based Nanostructures

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Funding:	$150,000

The goal of this project is to use crystallization of electronically conducting (conjugated) polymers to fabricate well-defined crystalline building blocks of nanometer-scale dimensions. These materials will then be assembled into photovoltaic devices with optimized structures and, therefore, improved efficiencies, in a cost-effective manner. It is well known that conjugated polymers often crystallize into nanowires or fibrils (i.e., one-dimensionally extended crystals with micrometer-scale lengths and nanometer-scale widths and thicknesses). We will study crystallization of a model conducting polymer, poly(3-hexyl thiophene) as a driving force for organization of several types of materials, including inorganic semiconductor nanoparticles, diblock copolymers, and segmented polymer nanowires. We will then determine how these nanowires of controlled structure can organize themselves into superstructures on larger length scales, and how organization of material on each length scale influences the photophysical properties of the resulting devices. On the fundamental level, our work will provide major impacts in the fields of optoelectronic materials and self-assembled nanomaterials by opening new routes to simultaneously control the organization and electronic properties of matter on three different length-scales: the molecular scale, the nanoscale, and the colloidal scale. On the applied level, our work will contribute to the critically important mission of improving efficiencies of low-cost polymer-based photovoltaic devices.

Interfacial Behavior of Polymers: Using Interfaces to Manipulate Polymers

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Funding:	$335,000

These studies focus on the manipulation of the structure and morphology of polymers using only interfacial interactions or the combination of interfacial interactions with an external field or confinement. The interactions between the segments of two polymers at an interface, the preferential interactions of the segments of polymers with a solid surface, or the difference in surface energies of polymers represent strong fields that can be used to control the orientation of polymer morphologies in thins films. In the case of block copolymers, these interactions lead to a directed self-assembly where the orientation of the arrays of nanoscopic domains have been shown to produce novel nanostructured films that have led to applications in the microelectronics and magnetic recording industries. External fields can also be used to overcome interfacial interactions generating non-equilibrium structures that provide pathways to addressable media where long-range lateral ordering and orientation of structures can be achieved. Developing strategies for such directed, self-orienting, self-assembling processes is one focus of the proposed studies. Internal fields, as for example ion complexation, will be used to impart rigidity to an otherwise flexible polymer that will be used to promote orientation and long-range ordering in thin polymer films. The incorporation of ions will, by default, produce a dramatic change in the dielectric constants of the components that will be used to enhance the influence of external fields in manipulating the morphology and in replicating patterns. In addition, the confinement of polymers within planar geometries and cylindrical pores, where the characteristic dimensions of the confining geometry are comparable to the characteristic length scales in the polymers, will be used to take advantage of commensurability conditions and forced curvature to manipulate the morphology in polymers and, in fact, generate structures that cannot be produced in the bulk at equilibrium. While model systems will be used, the findings in the proposed studies will be applicable to a much broader range of materials.

Symmetry Breaking for the Synthesis of Nanostructured Porous Materials

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Funding:	$237,000

The overarching theme of the project is to develop and deploy new methods for the synthesis of coordination polymers that can be used as high performance sorbents in applications such as efficient separations and high density fuel gas storage. The specific goals of the project can be broadly defined as those involving reduced symmetry linker design for producing coordination polymers and coordination polymers involving mixed linkers.

REDUCED SYMMETRY LINKER DESIGN

In the area of reduced symmetry carboxylate-based linkers, we have been able to synthesize a significant number of new linkers bearing coordinating groups not all related by symmetry elements. These in turn have led to the discovery of new coordination polymers when combined with earth abundant metals. With more structures in hand we have found that in addition to non-interpenetrated structures that are overrepresented in this class of coordination polymers, we are starting to generate interpenetrated structures when the metal cluster and ligand geometry are appropriately matched. In one case, we hypothesize this assembly mode has become accessible because a new metal cluster is generated. This cluster had not been observed before in either molecular or extended structures and is another key validation of the reduced symmetry linker approach in that, as a result of unequal edges of the linkers, new metal clusters are generated in order to satisfy (1) the coordination requirements of the transition metal and (2) the geometrical constraints of forming an extended, uniform structure. Building additional understanding of these cases is a key to both exploiting the novel properties of such clusters and to establish more firmly the geometric requirements to thwart interpenetration and generate high surface area materials.

COORDINATION COPOLYMERIZATION

In the realm of coordination copolymerization we have continued to focus on our new findings that materials arising from two or more linkers with identical coordinating functionalities can yield extremely high porosity. One exciting new direction was uncovered in a highly defective coordination copolymer in which minor ligand incorporation, although unable to alter the gross structure, lead to defects. These defects turned out to be ideal handles for the selective introduction of metals and the function of this material in catalysis was very recently demonstrated.

Spectroscopic Studies of Materials for Electrochemical Energy Storage

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Funding: $180,000

In the roughly 13 months that this grant has been in effect, we have made progress along several fronts described below.

(1) We have demonstrated the effect of magnetic field alignment of cast films of polymer electrolytes using wide-line ^{7}Li NMR. A paper was published in *Electrochimica Acta*.

(2) We successfully undertook a collaborative study (with U. Paris-Sud and U NC/Chappell Hill) of ionic transport in novel ionic liquids. The DCTA and DCA anions consist only of carbon and nitrogen, therefore natural abundance ^{13}C NMR was used to measure anion self-diffusion coefficients using standard pulsed field gradient methods, but with a lot of signal averaging! This is the first reported use of such methods in ion conducting media. A manuscript has been submitted to the *Journal of the American Chemical Society*.

(3) We have obtained single crystal NMR rotation spectra for $LiFePO_4$ and $LiCoPO_4$ which allows complete mapping of the magnetic susceptibility tensor in the vicinity of both the ^{7}Li and ^{31}P nuclei. One of the surprising results to come out of this work is that there is evidence for both through-bond and though-space interactions with the transition metal ion, whereas previous studies of polycrystalline samples reported by other groups emphasized only the through-bond couplings. A presentation was given by the DOE-funded postdoctoral fellow, Dr. Paul Sideris at a special meeting on Phosphates at Argonne National Lab, and a paper on this is being submitted to the Journal of the American Ceramic Society.

(4) We have begun work on BiF_3 conversion cathodes (with lithium anodes), in collaboration with Rutgers Univ. The focus is on the ultimate fate of the organic electrolyte solvents, and we have obtained ^{13}C enriched solvents for this purpose.

Bimetallic Electrochemical Displacement Materials Yielding High Energy, High Power, and Improved Reversibility

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Funding:	$200,000

POTENTIAL PROJECT IMPACT

This project will fundamentally advance the three key performance metrics for energy storage: energy density, power delivery, and reversibility.

HIGH ENERGY DENSITY

Currently, most battery cathode materials transfer of 0.5 to 1.0 electrons per formula unit, such as: $LiCoO_2$ (0.5 e^-, 155 mAh/g), $LiNiO_2$ (0.5 e^-, 200 mAh/g), $LiFePO_4$ (1.0 e^-, 170 mAh/g). The proposed materials will transfer multiple electrons per formula unit, providing opportunity for improvement in theoretical energy density.

HIGH POWER CAPABILITY

Phosphates have been successfully implemented as cathodes in lithium based batteries with the most notable recent success being lithium iron phosphate, $LiFePO_4$. Phosphate materials have proven attractive due to their high thermal and chemical stability yielding improved safety and broader temperature performance windows over previous materials. However, a challenge to successful implementation is overcoming their typically low electronic conductivity. The novel materials studied here will form in-situ conductive metallic networks, providing a materials design approach that will enable the use of nanomaterials and enhance energy density. The metal ion that is reduced to the metallic state will provide an in-situ conductive network which will enable the use of small particles by minimizing the inter-particle contact resistance. This should further enhance the discharge and charge rates of the composite electrodes.

REVERSIBILITY

The bimetallic family of compounds that we are proposing will provide multiple electron transfers per formula unit to yield high energy yet maintain a host molecular superstructure. Thus, the bi-metallic electrochemical displacement materials should facilitate the opportunity for enhanced electrochemical reversibility since the host superstructure will provide ion transfer channels.

METHODS TO BE EMPLOYED

Bimetallic electrochemical displacement reactions will be explored, where one ion (M) in a solid state material is reduced to the metallic state and the second metal ion (M’) undergoes electron transfer, yet serves to maintain a host structure. We propose to investigate bimetallic oxides, oxyphosphates and phosphorous oxides (MM’O, $MM'OPO_x$ and $MM'PO_x$). These material families provide rich compositional possibilities due to the presence of two metals as well as oxygen and phosphate structures. We have four broad objectives:

(1) Develop a new class of improved materials based on bimetallic oxides, oxyphosphates, and phosphorous-oxides: MwM'_xO_z, $MwM'_xOP_yO_z$, $MwM'_xP_yO_z$. The investigation will progress by (a) rationally identifying specific target compounds, (b) developing synthetic strategies to prepare the materials, and (c) conducting detailed chemical and physical characterization of the materials.

(2) Conduct electrochemical evaluation of the prepared materials to determine energy density, electrochemical reversibility, and power capability.

(3) Determine the reduction/oxidation mechanisms of the materials.

(4) Evaluate suitability of these materials as electrodes in energy storage devices.

Fundamental Science of High Open Circuit Voltage Excitonic Solar Cells

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Funding:	$250,000

During fiscal year 2011, we have finished and published the initial measurements of the miscibility of phenyl-C61-butyric acid methyl ester (PCBM) with poly(3-hexylthiophene) (P3HT)and poly(2-methoxy-5-(30,70-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV). We found that, while no intercalation occurs in P3HT crystals, amorphous portions of P3HT and MDMO-PPV contain significant concentrations of PCBM, calling into question models of bulk heterojunction solar cells based on pure phases and discrete interfaces. Our results suggest that current models of charge separation and transport must be refined. We have followed up these important results by measuring miscibility in a number of other systems and have shown that miscibility is a universal aspect of organic solar cells. Our measurements thus require a redefinition of the paradigm of bulk heterojunction solar cells used for many years; and we are in the process of developing such a new paradigm and about the implications of the miscibility observed by us. Due to our important contributions to this area, we have been invited and have just submitted a perspective on this topic to the *Journal of Physical Chemistry Letters*, which will be published in a special issue focusing on organic devices.

We have also achieved significant results in relating device morphology to solar cell performance in two widely studied and important all-polymer solar cell systems, including the system that presently holds the all-polymer solar cell efficiency record. The results have been submitted for publication in *ACS Nano*.

We have collected data on a number of important device systems, including 8.4% and 7% devices with high fill factor. Our soft x-ray scattering methods are unique and we have collected excellent data, which is presently being analyzed and indicates significant results. Surprisingly, in many systems investigated, the dominant domain size is ~80-100 nm, and thus much larger than the ~10 nm length scale set by the exciton diffusion length and often assumed to be the required domain size for optimal performance. In contrast to this, we find that many systems exhibit a hierarchy of length scale, which seems to help them be very efficient.

Great progress has also been made in using polarization dependent soft x-ray scattering for the characterization of organic devices in general and organic solar cells in particular. This method is sensitive to bond orientation anisotropy and we have shown that there is an in-plane molecular orientation structure even in the amorphous parts of the polymeric component in bulk heterojunction solar cells. Furthermore, this orientation is patterned by the dispersed component in the two component active layer. The polarization dependent soft x-ray scattering method developed by us is the only tool that can measure such orientation.

Linking Ion Solvation and Lithium Battery Electrolyte Properties

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Funding:	$178,000

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-LiX 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 (EC) and a linear carbonate such as ethyl methyl carbonate (EMC), has undergone only minor changes over the past 18 years. 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 (PHEVs)]. 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 the work by other researchers. This will in effect optimize multi-solvent electrolytes and efforts 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.) for electrolytes on demand.

These three research thrusts include (1) the exploration of the ionic association behavior of select LiX salts with a wide variety of solvents, (2) the conduction of an in-depth analysis of the thermal phase behavior of diverse solvent-LiX mixtures, and (3) the determination of electrolyte physicochemical and electrochemical properties for comparison with the ionic association and phase behavior.

Thrust 1 involves the develop a Li^+ Solvation Scale for Solvents by directly examining Li^+...anion interactions in a wide variety of solvents to determine which types of solvates exist in solution, i.e., solvent-separated ion pairs (SSIPs), contact ion pairs (CIPs) and aggregates (AGGs) in which the anions remain uncoordinated (to a Li^+ cation) or are coordinated to one or more cations.

Thrust 2 consists of the creation of a library of binary solvent-LiX phase diagrams. This is highly informative when combined with the ionic association information provided by Thrust 1. Numerous solvate crystal structures have been determined to provide insight into the manner of Li^+...solvent and

Li^+...anion coordination and to serve as model compounds for the Raman spectroscopic analysis used in Thrust 1 to determine the degree of ionic association.

Thrust 3 consists of determining a variety of solvent-LiX electrolyte properties over a broad temperature and concentration range including conductivity, LiX salt diffusion coefficients, viscosity and density. This, in combination with the information from Thrusts 1 and 2, will result in a comprehensive understanding of electrolyte/battery composition-property-performance relationships which is essential for the rapid formulation of improved electrolyte materials for new battery chemistries. Through collaborations, this work is being integrated with molecular simulations to greatly aid in understanding electrolyte solution structure. This work clearly delineates which solvent and anion structural features are critical for determining electrolyte bulk properties and how these properties are interrelated.

Theoretical Studies of Surface Reactions on Metals and Electronic Materials

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Funding: $143,000

This research is a theoretical research program on the structure and reactivity of molecules adsorbed on transition metal surfaces. A new direction of the work extends investigations to interfaces between solid surfaces, adsorbates and aqueous solutions and includes fundamental work on photoinduced electron transport into chemisorbed species and into solution. The goal is to discover practical ways to reduce water to hydrogen and oxygen using radiation comparable to that available in the solar spectrum. The work relates to two broad subject areas: (1) photocatalytic processes and (2) production of hydrogen from water. The objective is to obtain high quality solutions of the electronic structure of adsorbate-metal-surface-solution systems so as to allow activation barriers to be calculated and reaction mechanisms to be determined. An ab initio embedding formalism provides a route to the required accuracy. New theoretical methods are being developed and will be implemented in order to solve the large systems involved in this work. Included is the formulation of a correlation operator that is used to treat localized electron distributions such as ionic or regionally localized distributions. The correlation operator which is expressed as a two-particle projector is used in conjunction with configuration interaction.

Actinide Transition-Metal Chalcogenides and Pnictides

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Funding: $70,000

The overall objective of this grant is to increase our knowledge and understanding of Th, U, and Np solid-state chemistry.

More specifically, the objectives are to synthesize new transition-metal chalcogenides and pnictides of these actinides, to characterize them structurally, to determine selected physical properties, and to develop theoretical insights into these properties. Whenever possible, only compounds that we can characterize by single-crystal methods have been studied. Physical properties measured have included optical band gaps, magnetic susceptibilities, specific heats, and transport properties. In collaboration with Prof Donald Ellis, some DFT and related calculations have been performed.

Detailed results on $UFeS_3$ and $UFeSe_3$, UCuOP and NpCuOP, Np_3S_5 and Np_3Se_5, $Tl_3Cu_4USe_6$ and $Tl_2Ag_2USe_4$, and three complex neptunium thiophosphate compounds have been published.

Our present work on U has led to a number of new compounds, many of which have new structure types. These include the $A_2UM_3Q_6$ and $A_2U_6M_4Q_{17}$ compounds where A = alkali metal, M = Pd or Pt, and Q = S or Se. Dr. Eun Sang Choi of the National High Magnetic Field Laboratory at FSU has studied the magnetic properties of these compounds and obtained some very interesting preliminary results.

Our present work on Th compounds includes the syntheses of the new ternary compounds $Rb_2Th_7Se_{15}$, Th_2GeSe_5, and $ThLn_2S_5$ (Ln = Y, Tb, Er), and the new quaternary compounds $TlCuThSe_3$ and $TlThSb_2Se_6$. Theoretical DFT calculations of electronic structures on the compounds AnQ, AnQ_2, and AnOQ (An = Th, U, Np, Pu; Q = S, Se, Te) are being made. The calculated optical band gaps will be compared to our experimental results.

Our work on Np compounds has been stalled for more than eight months owing to numerous non-scientific problems at Argonne National Laboratory.

Chemistry and Properties of Complex Intermetallics from Metallic Fluxes

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Funding:	$150,000

This project investigates the reaction chemistry and synthesis of 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 (i.e., liquid aluminum, gallium, and indium). We focus on the ability of these fluxes to produce phases which are difficult to predict a-priori and are likely to feature novel characteristics. Specifically, we seek to:

(a) Discover mainly Si (or Ge)-based compounds with new structures, bonding, and exotic physicochemical properties. The aim is to discover exciting new materials displaying unusual bonding and enhanced cooperative phenomena, such as magnetic ordering, phase transitions, spin and charge density waves, as well as other properties, such as oxidation resistance.

(b) 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.

(c) 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.

This project will enhance our basic knowledge of the solid state chemistry and physics of intermetallics, enable us to produce new materials with unusual or enhanced bulk properties, and ultimately help improve our understanding of component/matrix interactions that could lead to better Al-matrix alloys.

This work will be performed predominantly with graduate students, which will help ensure the availability of future scientific talent trained in the important area of solid state and materials chemistry. The new knowledge to be generated in this project will have scientific impact not only in materials chemistry and condensed matter physics but also in other areas of science and technology, including those where new coatings and materials are needed to operate in extreme environments.

Materials Science of Electrodes and Interfaces for High-Performance Organic Photovoltaics

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Funding:	$533,334

Research and development in organic photovoltaic (OPV) cells have made impressive advances over the last three years with laboratory cell efficiencies now reaching 9%. The upper limit of light to power conversion efficiency for single layer OPVs as predicted by theory is ~23%. Organic cells offer a very low-cost, readily manufacturable, and durable solar power for a wide range of in-door and out-door applications. With further effort, the vision of OPV cells replacing the current generation of inorganic solar cell systems may become a reality. Further gains in efficiency and durability, to that of competitive, high-performance inorganic photovoltaics, will require effort and breakthroughs in transparent electrode and interfacial materials science and engineering. This project pursues an integrated basic research program by an experienced and highly collaborative interdisciplinary team of five principal investigators with expertise in solid-state materials chemistry, organic materials, quantum theory, solar cell fabrication and characterization, microstructure fabrication, and low temperature processing. This team will address in unconventional ways, critical electrode-interfacial issues underlying OPV performance —controlling band offsets between transparent electrodes and organics, addressing current loss/leakage problems at interfaces, and new techniques in low temperature and large area cell fabrication to minimize cost. The proposed research foci are (1) the design (based on theory) and synthesis of advanced TCO layers with high conductivity and transparency but without (or minimizing) the use of Indium, (2) the development of a theory-based understanding of the best configuration for the ideal interface between oxide electrodes/interfacial layers and OPV hole-transporting organic molecules/polymers, and (3) the exploration and development of new processing techniques and cell architectures for the next generation of large-area flexible OPVs. The goal is to develop for the academic, national laboratory, and industrial photovoltaic community, the fundamental scientific understanding needed to design, fabricate, prototype, and ultimately test and commercialize high-efficiency OPV cells incorporating these new concepts.

Research Project on the Recruitment, Retention, and Promotion of Women in the Chemical Sciences

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Funding:	$160,000

Energy is the lifeblood of the U.S. economy. It could also become the “Achilles’ heel” of the nation’s economy if it continues on the path of relying on imported oil and environmentally damaging energy resources to fuel its economy. Consequently, the development of new energy resources and technologies that are efficient, environmentally benign and affordable has become a key component of DOE’s strategy for meeting the nation’s future energy needs. Innovative advances in this area require that DOE recruit the best and brightest to participate in this exciting and challenging science and technology endeavor, and to provide them with a workplace environment where the best ideas can flourish and grow. Currently this nation is far from reaching its recruiting potential in science, technology, math and engineering (STEM) fields, particularly from underrepresented groups such as women and minorities. In the field of Chemistry where women today earn 30% of the Ph.D. degrees, only 15% of the chemistry faculty at the top 50 most research active universities are women. In materials science and engineering (MSE), 13% of the faculties are women while 26% of the Ph.D. and 28% of the B.S. degrees are granted to women. In physics, women occupy only 9.5% of the faculty positions across all ranks at the major research universities. This low representation of women in leadership positions at research universities is also a problem at the DOE National Laboratories where only 11% of scientific directors and 3% of directors and deputy directors are women.

In recognition of the need for a more diverse workforce in its DOE funded research programs, in 2000 the Basic Energy Sciences (BES) of DOE began funding a unique new research based program called “COACh” (Committee on the Advancement of Women Chemists) that is developing programs to increase the number and success of women chemists and chemical engineers. Since this initial funding from BES, COACh has grown into an internationally recognized organization that has had a positive impact on the careers of over 400 women chemists and several thousand other women scientists and engineers in the fields of physics, engineering, math, computer science, materials science, geology and biology. The initial DOE funding also gave credibility to COACh efforts that lead to other agencies, the National Science Foundation and the National Institutes of Health, to join in and help fund other COACh activities in a partnership.

This proposal seeks continued BES funding for COACh activities that are targeted towards increasing the recruitment, retention and advancement of all that seek careers in STEM fields, particularly those from underrepresented groups. The proposed projects build on the successful COACh activities of the past 8 years, and continue the expansion of its programs to other STEM fields beyond the initially targeted chemistry community. The proposed projects have the goals of (1) understanding through research the factors that are responsible for the lower representation of women in the STEM workforce and the barriers that are slowing their career pace relative to their male colleagues; (2) using the research to design and implement professional training, mentoring, and networking programs for women faculty, graduate students, and postdoctoral associates that will increase their ability to achieve their career goals; and (3) using the results of this research to develop and deliver programs to all faculty, department chairs, and research center directors that create a laboratory atmosphere that is inclusive, supports diversity, and enhances scientific innovation.

Wet Interfaces: Molecular Processes Underlying the Structure and Assembly of Thin Films and Nanoparticles at Complex Interfaces

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Funding:	$261,000

As a nation we face a multitude of challenges in our quest to develop sustainable and environmentally benign energy resources for today and for future generations. Developing more efficient ways to recover and use our existing fossil fuels, minimizing and sequestering excess green house gases resulting from their usage, developing new alternative energy resources and increasing the efficiency of current sources are all at the top of the “to do list” of challenges we face. Materials chemistry has a leading role to play in these areas as well as in addressing many other important societal issues that rely on advanced technologies. Many exciting advances in materials chemistry have been made in the past decade towards the development of new materials, in the area of molecular architecture and nanoscience, as well as in the development of new “bio-inspired” materials that seek to emulate materials that have evolved in nature. Many of these new materials are being made in more complex and reactive environments than in the past where vacuum or clean-room conditions were traditionally used. The assembly of thin films at liquid/solid and liquid/liquid interfaces fall into this category as well the multitude of unique nanostructured materials that assemble in solvents and at liquid 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 molecules at these interfaces.

The focus of the proposed studies is on obtaining a molecular level picture of how surfactants, nanoparticles and macromolecules adsorb and assemble from aqueous solution to molecular and substrate surfaces. The studies will (1) examine the molecular structure and dynamics of interfacial constituents during the assembly of surfactants and charged polymers from aqueous solution to interfaces, (2) measure the competitive and synergistic effects of mixed surfactant and polymer systems as they adsorb and desorb at these interfaces, and (3) provide new insights into the molecular structure of surfactants and macromolecules adsorbing to mineral particle surfaces, and the characteristics of these coated particles in liquids and at liquid surfaces. The fundamental studies to be pursued have direct relevance to many important areas of interest to DOE, including oil recovery, environmental remediation, surface wetting, flotation, nanoparticle assembly, and biomolecular assembly. The proposed projects build on some exciting new discoveries that we have made during the current funding period, particularly in the areas of polymer and particle adsorption at surfaces. We will employ a variety of new and existing experimental techniques including surface vibrational sum frequency spectroscopy (VSFS), Raman spectroscopy, infrared reflection adsorption spectroscopy (IRRAS), atomic force microscopy (AFM), contact angle, scanning electron microscopy (SEM), surface tension and zeta potential measurements.

Bi-Continuous Multi-Component Nanocrystal Superlattices for Solar Energy Conversion

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Students:	3 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding:	$732,000

Our SISGR team is exploring the synthesis and assembly and electrical and optical properties of three-dimensional nanocrystal (NC) superlattices, comprising combinations of NCs that self-organize into well-defined, crystalline architectures. We are focusing on crystal structures having bi-continuous, NC sub-lattices assembled from n and p-type semiconductor NCs that will form type-II energy offsets to drive charge separation onto electron and hole transporting sub-lattices and provide wide coverage of the solar spectrum. Wet- synthetic methods were advanced to achieve high quality, monodisperse II-VI and IV-VI NCs, tunable in NC size and shape, that form the building blocks for our studies of NC superlattice assembly and of charge transfer and transport and emission and energy transfer. We developed a method to assemble NCs and transfer NC membranes, composed of single or multi-component NC superlattices, from a liquid surface and then integrate them onto surfaces and into functional electronic devices, with uniformity over large, centimeter squared areas. Slow drying of the NC dispersion forms membranes tunable through concentration to be as thin as a NC monolayer, whereas fast drying gives rise to instability in the drying front and oscillatory NC deposition forming periodically striped, NC membranes. We have also developed the thiocyanate and its analogs, selenocyanate and selenourea, as surface capping groups for NCs. The thiocyanate allows the NCs to be stable in solvents for NC film deposition or for exchange of NC assemblies in the solid state. We have shown that the short interparticle spacing provided by the thiocyanate allows for strong interparticle coupling and the realization of facile band-like transport, giving rise to high carrier mobilities and to-date, to the highest reported photoconductivities in NC arrays.

We are applying non-linear optical Kerr gating and time-correlated single photon counting to probe quenching observed in these more strongly coupled NC assemblies. Combining the liquid phase assembly of PbS nanocubes and the mild processing conditions afforded by the thiocyanate, we realized the first quantum-dot based circuits on flexible plastic substrates. In periodically striped NC assemblies, we spatially-resolved enhanced photoconductivity in thicker NC regions, that are interesting for large interfacial area solar cells. Using the liquid-air interfacial assembly process, we demonstrated that three distinct NC components assemble into ternary NC superlattices, setting the stage for studies of bi-continuous semiconductor NC sub-lattices with isolated plasmonic NCs to enhance NC absorption. We have shown through simulation that enhanced absorption in semiconductor NCs may be realized through the use of plasmonic resonance as the NCs are arranged in close proximity to metal nanoparticles in the architectures of metal core- semiconductor shell NCs and in multi-component NC superlattices. We have demonstrated using continuous wave and time-resolved optical spectroscopies that plasmonic resonance acts to enhance optical processes in the absorption and emission of nanostructured materials. We are combining structural, optical, and electrical measurements to probe charge transfer and transport and emission and energy transfer at the length scale of the NC in multi-component NC superlattices using scanning probe and transmission electron microscopies and at shorter time scales using ultra-fast optical spectroscopies.

New Superconducting Materials

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The superconducting materials program at Princeton has recently begun looking carefully at a new track for finding new superconductors, based on chemical reasoning to choose which elements to try in combination. Purely ionic compounds such as NaCl and Al_2O_3 have localized electrons and are insulating, making them a poor choice when looking for superconductors. Intermetallic superconductors are the most common superconductors such as Nb, Nb_3Sn, $RhSn_2$, $AuPb_2$, and $NiZr_2$ but they tend to have low transition temperatures (T_c; 9 K, 18 K, 0.6 K, 3.1 K and 1.52 K respectively). Compounds with a balance between metallic and ionic character are more rarely superconductors but they can be more interesting in that they can have higher transition temperatures. For example the high T_c copper oxide superconductors, such as $YBa_2Cu_3O_7$, have a mix of ionic and covalent bonding while they still have a partially filled band at the Fermi level. The iron arsenide superconductors, which also have both ionic and covalent bonding character, have high T_c's as well. For example in LaOFeAs the LaO sheets have ionic character and the FeAs sheets have more covalent character. When this compound is doped with fluorine it becomes superconducting at 26 K. With these compounds in mind, we believe that it is reasonable to examine other compounds with a mixture of ionic and covalent character that are still metallic.

Sulfur, with its electronegativity of 2.5 on the Pauling scale, has a mid-level electronegativity. Combining it with an early transition metal (e.g., Nb, electronegativity 1.6) and another transition metal would lead to a compound with a partially ionic character, which may lead to interesting superconductors. Quite a few binary metal rich sulfide superconductors are currently known, supporting our idea. Therefore in our DOE-sponsored program in superconductivity we are looking for new superconductors and new compounds in the high temperature phases of ternary metal rich sulfides. We are systematically performing reactions with combinations of three elements and testing them for superconductivity. One of those elements is sulfur, the second element is an early transition metal (Zr, Nb, Mo, Hf, Ta or W), and the third element is a first or second row transition metal from the mid to late columns in the *d*-shell filling series. Reactions are being performed in an arc melter and on annealing at 1400° - 1600° C in tantalum tubes to reach the high temperatures needed.

Basic Surface Chemistry and Physics of Carbon-Based Electronic Materials Modified by Silane Molecular Layers

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Funding: $133,000

The main focus of this project is the study of physical and chemical aspects of the new class of phenomena that we have discovered in 2008 – the molecular self-assembly at the surface of carbon-based electronic materials, such as organic semiconductors, carbon nanotubes and graphene. It's been realized that growth of self-assembled monolayers (SAM) at these surfaces is possible, and it results in a high surface conductivity due to mobile holes induced by the SAM in the semiconductor. Since a postdoctoral fellow joined the group to work on this project in February 2011, we have had a great deal of progress.

Mitigating Breakdown in High Energy Density Perovskite Polymer Nanocomposite Capacitors

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Funding: $150,000

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 hybrids to plug-in hybrids 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 challenge 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 (target E_{bd} >250 V/μm), while the inorganic filler delivers the desired dielectric characteristics (target ε' >350). The fundamental challenge for these composites lies in aggregation of the inorganic filler at the percolation threshold (~15-20 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 challenge, 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.

Design Principles for Nanomagnets Based on Molecules: Investigation of Effect of Spin, Orbital & Molecular Shape Anisotropies

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Funding:	$240,000

Efforts to engender bi-stability in clusters incorporating late first-row transition metal ions have focused primarily on increasing the ground-state spin value (S) to raise the thermal barrier for spin reorientation, but success has been limited. A less well-explored avenue to increasing the blocking temperatures of 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. The synthesis of new clusters, guided by this premise, and the assessment of their structural, electronic, and magnetic properties constitute the foundation for our proposed research. The continuing interest in bistable complexes arises from their potential use in high density data storage, quantum computing, and as sensors and switches in molecular electronic devices. Bistabilty can arise from slow paramagnetic relaxation of the magnetization as well as by thermally- or light-induced charge transfer and/or spin crossover events. Our DOE funded project thus far has led to the development of new clusters that exhibit remarkable properties and which have provided us insight into the complex interplay of metal ion, ligand, and intermolecular interactions with solvent and supramolecular interactions that affect the properties of these materials. During the course of the last grant period, we isolated a linear trimer based on Os(III) hexacyanide and Mn(III) with Schiff base ligands that exhibits exchange-biased single-molecule magnetic (SMM) behavior due to extensive intermolecular interactions, the first such evidence for this phenomenon in cyanide based SMMs. This result provides us with an ideal platform to probe the effect of ligand and counterion variations on the bistability of a small magnetic unit. We have also incorporated 4d and 5d cyanometallates (Os(III), Ru(III) and Mo(IIII) into trigonal bipyramidal clusters of the type ($[M(tmphen)_2]_3[M'(CN)_6]_2$, resulting in the first ferromagnetic interaction observed between Mo(III) and Co(II)/Ni(II) through cyanide and the cluster $[Fe(tmphen)_2]_3[Os(CN)_6]_2$, which undergoes a thermally-induced reversible intramolecular electron transfer and was recently highlighted in Nature Chemistry. Efforts by our group have also yielded new structures incorporating $[Mo(CN)_7]^{4-}$, namely two new octahedral clusters ($[M(tmphen)_2]_4[Mo(CN)_7]_2$•(solvent); M = Cr(II), Mn(II)) with possible SMM behavior and an extraordinary docosanuclear cluster that holds the record for the highest ground state spin value of any cyanide-bridged cluster known to date, a molecule featured on the cover of Angewandte Chemie. We plan on expanding the families of our trigonal bipyramidal, octahedral, cubic, and linear trinuclear molecules to include more 4d/5d metal ions as well as early 3d metal ions, efforts that will be guided by theoretical models. The use of various synthetic techniques, including anaerobic methods, and the characterization of products using a wide range of tools, including XRD, EPR, and magnetic analyses and infrared, electronic, and Mössbauer spectroscopies, provides a broad education for all students and postdoctoral researchers involved in the project and prepares them well for multidisciplinary research.

The Synthesis, Structures, and Chemical Properties of Macrocyclic Ligands Covalently Bonded into Layered Arrays

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Funding: $60,000

Our goal is to investigate separations based upon a new class of porous layered nanoparticles. These compounds have been found to reject or have a very low affinity for monovalent ions, low affinity for divalent ions and high selectivity for tri- and tetravalent ions. We have found that K_d values of $10^5 – 10^6$ are obtained for lanthanides at pH of 3-3.3 and much lower with more acidic solutions. Thus, group lanthanide separations from other ions have been effected. We are now investigating separations of lanthanides from actinides by oxidizing the actinides to higher oxidation states to obtain yl ions of charge +1 or +2. We have been able to oxidize Pu, Np, Am in this range and will carry out separations in the next two months at Los-Alamos, Carlsbad. Separation of Am iron Cm is a distinct possibility. Other separations are in the planning state.

The question to be answered is why do these porous zirconium and Sn(IV) phosphonates behave in this manner? Because they are amorphous, we have to use unconventional methods of structure determination. We are initiating a program of obtaining structural information by utilizing EXAFS and atomic pair distribution functions. In addition, we have prepared similar but not identical compounds of aluminum as fine powders with a reasonable X-ray powder pattern. We are in the process of solving this structure and examining the ion exchange behavior of this aluminum compound.

Extracting Hot or Multiple Charge Carriers from Photoexcited Semiconductor Nanocrystals

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Funding: $210,000

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, where quantization in electronic structure may slow down hot carrier cooling. To realize the potential of the hot carrier solar cell from semiconductor nanocrystals, two more conditions must be met: (1) "hot" carrier transfer from a photoexcited semiconductor NC to an electron or hole conductor must be competitive with cooling within each nanocrystal and (2) the hot carrier transfer process must occur in a very narrow energy window. During the last funding period, the PI and coworkers have successfully demonstrated the first condition. Using time-resolved optical second harmonic generation (SHG), the PI's team showed unequivocally that hot electron transfer from semiconductor NCs (PbSe) to a widely-used electron acceptor (TiO_2) is indeed possible and, with appropriate chemical treatment of the nanocrystal surface, occurs on a much faster timescale than previously expected (within 50 fs). The objectives of the research in the current funding period are two-fold: (1) to further establish the fundamental physical mechanisms in hot electron transfer from photoexcited NCs to the TiO_2 electron acceptor and (2) to explore the possibility of energy selective hot electron transfer through control of interfacial electronic energy landscape by core-shell structures and molecular linkers.

Improved Electrical Energy Storage With Electrochemical Double Layer Capacitance Based on Novel Carbon Electrodes, New Electrolytes...

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Funding:	$453,000

Our team is studying the interplay between graphene-based and graphene-derived carbons as the electrode materials in electrochemical double layer capacitors (EDLC) systems on the one hand and electrolytes including novel electrolytes such as newly synthesized ionic liquids (ILs), on the other. We have made important advances including a paper published in *Science* in 2011 (team led by Ruoff) that describes a new type of carbon with atom-thick walls and a distribution of mesopores and micropores that favors high gravimetric capacitance and high electrical energy storage on a gravimetric basis, with both organic or IL electrolytes. This carbon is made by KOH-activation at 800 ^{o}C under flowing argon gas of microwave-exfoliated graphite oxide (MEGO), and is thus referred to as 'activated MEGO' or 'a-MEGO'. This effort included co-authorship by scientists from the Brookhaven National Laboratory (Drs. Eric Stach and Dong Su) who contributed high resolution transmission electron microscopy and electron energy loss analysis (EELS) of the carbon. In addition to synthesizing and studying new carbons such as a-MEGO as electrode candidates, our team has had strong efforts in solid state NMR, synthesis and characterization of new ILs, in study of the interaction between ions in the electrolytes and the carbon materials, and in fundamental theory of EDLC.

Some examples of a wide range of efforts underway by our team include investigating the effect of interactions of azolium azolates (Rogers) type ionic liquids (ILs), namely [BMIM][4,5-dicyanoimidazolate] and [BMIM][2-methyl-5-nitroimidazolate], with graphene and graphite for potential use in advanced battery and ultracapacitor applications. The aromatic character of both cation and anion rings is an important tool for enhancing the interactions of the ionic liquids with graphitic surfaces. We have also focused on the synthesis (Bielawski) of a broad range of ionic liquids (ILs) for applications in electrochemical double layer capacitors (EDLCs). Exploring and varying both the structures of the cations and anions, the former incorporated into these ILs include cyclic and acyclic ammonium, N,N-dialkylimidazolium, and N-alkylpyridinium species; anions studied include various halides (Cl, Br, I), tetrafluoroborate (BF_4), hexafluorophosphate (PF_6), trifluoromethanesulfonate (triflate; OTf), bis(trifluoromethanesulfonyl)imide (bistriflimide; NTf_2), and methylsulfate ($MeSO_4$). To explore the nature of the oxygen interactions (covalent vs. non-covalent) in thermally reduced graphite oxide (TRG), initially intercalated with ionic liquids (ILs) synthesized by our team, we (Chabal) have studied the intercalation of an extensive number of ILs. Based on the spectroscopic findings, particular attention has been paid to three selected ILs: (1) N-methyl-N,N,N-tris(2-hydroxyethyl) ammonium iodide; (2) N-methyl-N,N,N-tris(2-hydroxyethyl) ammonium methyl sulfate; and (3) N,N,N-tributyl-N-octyl ammonium methyl sulfate.

Other efforts include the use of solid state NMR (SSNMR), such as for the study of the chemistry and molecular-level structural changes in the production of chemically modified graphenes by chemical reduction of 13C-labeled graphene oxide with 15N-labeled hydrazine by high-resolution ^{13}C and ^{15}N SSNMR (Ishii). This allowed identification of ^{15}N species having ^{15}N chemical shift of 190 ppm, which was likely incorporated from ^{15}N-labeled hydrazine to the edge of the graphene sheet. During the 2011 fiscal year Sandia (Alam) has continued to provide NMR characterization of the unique ionic liquids (IL) being developed by the Bielawski group, and the graphene nanocomposites developed by Ruoff group. This NMR effort has resulted in two published manuscripts in 2011. In the upcoming year our efforts are directed towards the combining of pulse field gradient (PFG) NMR experiments to measure self-diffusion constants as a function of temperature and the recently published ^{14}N NMR relaxation experiments to gain further physical insights into the molecular associations in IL. These experiments are being extended to probe the interaction of IL on surfaces, including graphene. More recently we have begun development of solid state 14N MAS NMR experiments to look at the dynamics in solid IL, and the impact of surface association on local dynamics.

Our theoretical effort (Hwang) focuses on investigating the structure and capacitance of electric double layers (EDLs) at the interface between ionic liquids (ILs) and carbon-based electrodes, with particular attention to the effects of the size and chemical functionality of IL anions and cations as well as the topological defects, functionalization, and geometric factors of sp^2-bonded carbon electrodes. Since the EDLs are truly molecular phenomena, atomistic simulations can be very helpful in elucidating their microstructure and properties.

Materials and Interfacial Chemistry for Next-Generation Electrical Energy Storage

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Funding:	$700,000

The challenges facing rechargeable batteries are limited energy density, cycle life, and rate of charge within the limits of safety and cost constraints. The energy density has two components: voltage and capacity. To increase the rate of charge without the danger of plating of lithium on the anode and, at the same time, to increase the anode capacity, we are developing nanoparticle alloys buffered by carbon and nano-oxides that give a voltage $0.5 < V < 0.8$ V versus lithium. To increase the voltage of the cell to V

> 4.0 V with these anodes, we are investigating how to stabilize at 60 °C layered-spinel cathodes containing Ni^{2+} and Mn^{4+}, which provide voltages up to 4.8 V versus lithium; formation of a cathode SEI layer sets in above 4.3 V. This problem involves tailoring the chemistry at the electrolyte/cathode interface. However, the specific capacity of a cell is limited by the solid-solution range of Li in the host cathode structure, and formation of a Li^+-permeable passivating SEI layer on the anode surface introduces an irreversible loss of cathode capacity in the initial charge. To alleviate this loss and to enable alternative cathode strategies, we are investigating the use of a solid Li^+ electrolyte as separator. This strategy requires identification of an oxide Li^+ electrolyte having a conductivity sLi > 10-4 S cm-1 that is stable on contact with a lithium anode. For this purpose, we are investigating oxides with the garnet framework and with the NASICON framework. This strategy would allow a different liquid either side of the separator, and dendrites formed on a lithium anode would be blocked by the separator from reaching the cathode. Moreover, the Li^+ of the SEI layer on the anode would, with this configuration, come from the lithium anode, not from the cathode. If the solid Li^+-electrolyte separator is stable in water, it is possible to entertain a flow-through aqueous cathode or an air cathode. For these, we are investigating air electrodes in an acidic phosphate buffer catholyte as well as oxide catalysts for the oxygen-reduction and oxygen-evolution reactions. Finally, we are also investigating novel, low-cost synthesis of electrodes consisting of nanoparticles of different morphology. These activities are complemented by advanced materials characterization methodologies carried out in collaboration with the Oak Ridge National Laboratory.

Spectroscopy of Charge Carriers and Traps in Field-Doped Organic Semiconductors

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Funding:	$57,000

The proposed research aims to achieve quantitative and molecular level understanding of charge carriers and traps in field-doped organic semiconductors via in situ optical absorption spectroscopy, in conjunction with time-resolved electrical measurements. Organic semiconductor materials are central to a number of emerging technologies, such as organic photovoltaics (OPV), organic field effect transistors (OFETs), and organic light emitting diodes (OLEDs). In spite of substantial commercial and scientific momentum in the development of organic semiconductors, a clear understanding of the fundamental mechanisms responsible for charge-carrier transport in these materials is still lacking. This is especially true for OFETs that have undergone comparatively less development than OLEDs. OFETs are the key switching devices for plastic electronics and are essential for logic, signal amplification, and display control. Additionally, OFETs are excellent testbeds for probing electrical transport in organic semiconductors as a function of continuously tunable charge density. Current knowledge on field-doped charge carriers in OFETs comes predominantly from transport measurements. These measurements provide direct information on charge carrier mobilities and their dependences on molecular structures, film properties, doping levels (gate bias voltage), and temperature (thermal activation or the lack of). However, little is known about the physical/chemical nature of the charge carriers, particularly the molecular origin of charge carrier traps that are thought to be responsible for operational instability in OTFTs.

The long-term objective of the proposed research is to develop a quantitative and molecular-level understanding of charge carriers in OFETs, from the onset of conductivity at low VG, to the metal-insulator transition at high VG, and to the residual charge states (traps) when VG is switched to zero. Towards this end, the PIs will employ total internal reflection Fourier transform infrared (ATR-FTIR) and near-infrared (ATR-FTNIR) spectroscopies to directly probe the buried interfaces in operative OFETs fabricated on top of waveguides. Here, ATR-FTIR and FTNIR spectroscopy will provide direct information on charge carrying species from molecular vibrations that are distinctively different from those of the neutral species, as well as from electronic transitions within the band gap due to polarons and bipolarons. Complementary experiments from transient gate-current measurements will provide quantitative information on the amount of charge traps and the rate of de-trapping. The feasibility of this approach has been successfully demonstrated during the current funding period. Major achievements include (a) establishing electrostatic and electrochemical doping in perylene tetracarboxylic diimide (PTCDI), (b) demonstrating molecular control of electron injection barriers and density of states in PTCDI and chemically modified PTCDI, (c) observing charge carrier traps in the form of polarons and bipolarons in P3HT, and (d) quantifying trap density by displacement current measurements for single crystal OFETs. These initial successes have laid the foundation for the systematic approach proposed here. The specific aims are to (1) identify the chemical/physical nature and quantify the concentrations of residual charge carrier traps in organic semiconductors, (2) quantitatively correlate transport characteristics in OFETs with spectroscopic signatures of charge carrying species determined in situ and establish fundamental mechanisms for the insulator-metal transition at high doping levels in gate-doped P3HT, and (3) carry out comparative studies of high-capacitance molecular dielectrics, including polymer electrolytes, ion gels, and self-assembled nano-dielectrics.

Linking Ion Solvation and Lithium Battery Electrolyte Properties

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Funding:	$117,000

Ionic association is a key feature of solvent-salt systems. It has long been known that different forms of ionic species, i.e., solvent-separated ion pairs (SSIPs), contact ion pairs (CIPs) and aggregates (AGGs) form in which the anions remain uncoordinated (to a Li^+ cation) or are coordinated to one or more cations, respectively. In addition to solvent and anion structures, temperature and salt concentration also influence the types of solvate species present. Only very limited information is available in the literature regarding the ionic association state of electrolyte mixtures and the link between this and the electrolyte properties. Yet the electrolyte is both figuratively and literally the core of batteries, which, in turn, are the heart of portable electronics and plug-in hybrid electric vehicles (PHEVs). Frequently, the electrolyte is the bottleneck in achieving critical device performance criteria. Molecular-level electrolyte interactions govern material properties, but such interactions remain a murky, poorly understood and hardly studied topic despite the crucial role that the electrolyte plays in device power, low/high temperature operation, lifetime, safety, cost, etc. Under this program were are undertaking a detailed analysis of how solvent and anion structure govern the solvation state of Li^+ cations in solvent-lithium salt (LiX) mixtures and how this, in turn, dictates the electrolyte physicochemical and electrochemical properties and battery performance.

Optical, Electrical and Magnetic Studies of Conjugated Systems

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Funding: $210,000

This project is an experimental and theoretical research effort focused on the fundamental and applied science of pi-conjugated organic semiconductor systems including ordered and disordered polymer films, small molecules and polymer/fullerene blends.

Our synthetic goal is focused on incorporating 13C isotope in a variety of polymers and fullerene molecules. This isotope enhances the hyperfine interaction (HFI) of the injected carriers with carbon nuclei, thereby enhancing the spin-lattice relaxation rate. We explore the increased HFI on various optical and magneto-transport effects, and charge photogeneration in polymer/fullerene blends for photovoltaic applications. We also synthesize deuterium rich and Pt-rich polymers for further tuning the HFI and spin-orbit (SO) coupling, respectively.

Through optical, electrical and magnetic studies of pristine and blend of various pi-conjugated organic semiconductor with fullerene molecules, we investigate a number of fundamental scientific questions with important ramifications on potential applications of these materials. In particular, we address key aspects associated with the following processes: (1) the photogeneration of interchain photoexcitation species in ordered pristine polymer films, (2) the charge photogeneration in polymer/fullerene blends that form active layers in organic solar cells, (3) photoexcitation in Pt-rich polymers with enhanced SO coupling, (4) spin dynamics in pi-conjugated polymers that are active layers in OLEDs, and (5) the influence of HFI, SO interaction, and spin exchange on the magnetic-field response of organic diode devices. For these investigations, we use optical, electrical, and magnetic measurements, as well as appropriate theoretical modeling.

The inclusion of several projects that span a variety of science and engineering disciplines is a tremendous advantage in educating the next generation of scientists and engineers in the U.S.

Synthesis of Molecule/Polymer Based Magnetic Materials

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Funding: $237,000

The design/synthesis/characterization/exploitation of organic-based magnetic materials, and those combining magnetism with other technologically important properties (e.g., electrical, optical, and mechanical) is the research goal. These materials are important for future electronic/photonic devices, especially due to the need for reduced energy consumption and environmentally friendlier processing and disposal. The proposed 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. Our multidisciplinary research builds upon these and other accomplishments and targets the several projects to understand the structure-function relationship to ultimately enable the preparation of stable, technologically useful, high-Tc organic/polymer-based magnets.

Design and Synthesis of Chemically and Electronically Tunable Nanoporous Organic Polymers for Use in Hydrogen Storage Applications

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Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding:	\$190,000

The synthesis of nanoporous borazine-linked polymers (BLPs) featuring various 2-D and 3-D building units has been established using thermolysis reactions of arylamine-borane or arylamine-borontrihalide adducts in aprotic solvents. Pore surface chemical modification using H, Cl, and Br substituent on the boron sites leads to diverse textural properties and gas (H_2, CO_2, CH_4) storage and separation performance. BLPs have moderate to high surface areas (in the range of 600 to 2800 m^2 g-1) and can store up to 1.93 wt% of hydrogen at 1.0 bar and 77 K; as in the case of BLP-12(H), this value exceeds the performance of most organic polymers and is comparable to those of the best performing materials in the field such as MOFs under similar conditions. The isosteric heat of adsorptions for H_2, CO_2, CH_4 were performed using the virial method. In addition to their performance in gas storage, the gas selectivity of BLPs was investigated using initial slope calculations and the Ideal Adsorbed Solution Theory (IAST). Interestingly, one of the BLPs that feature chloride lined channels exhibit very high (28) CO_2/CH_4 selectivity, making this class of polymers interesting for CO_2 separation from natural gas.

We also have extended our efforts to synthesize a new class of functionalized porous organic polymers containing imidazol moieties in their pore walls and assessed their potential in gas separation and storage. We have shown that BILP-1, which is composed of tetraphenylmethane and triphenylene units linked together through imidazole ring formation, can store 4.3 mmol/g of CO_2 at 273 K and 1 bar; it also stores about 2 wt% of hydrogen at 77 K and 1 bar. Thus far, the performance of BILPs in gas storage are the highest by porous organic polymers reported to date under the aforementioned conditions. In addition to their gas storage, BILPs display very high CO_2/N_2 and CO_2/CH_4 selectivity, reaching 113 and 17, respectively, at 273 K and 1 bar, making them highly attractive in post-combustion CO_2 capture and natural gas purification applications. Worth mentioning is the chemical and thermal stability of BILPs; they remain intact in aqueous or acidic media and possess high thermal stability (~450 °C). High pressure gas sorption measurements are underway to evaluate the performance of both BILPs and BLPs in gas storage under elevated pressure and ambient temperature.

Molecular and Nanoscale Engineering of High Efficiency Polymer and Hybrid Organic/Inorganic Solar Cells

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Funding: $380,000

Despite rapid advances in device performance, the design rules for optimizing bulk heterojunction solar cells remain elusive. Improving open circuit voltage, harvesting more of the solar spectrum, and increasing fill factors are all obvious targets, but the pathways to achieve them are not clear. For instance, in both organic and hybrid organic/inorganic excitonic solar cells, donor/acceptor interfaces are used to dissociate excitons into free charges. Charge dissociation at these organic donor/acceptor interfaces is widely believed to proceed through an intermediate “charge transfer exciton” state in which the electron has transferred from the donor material to the acceptor, but in which the electron and hole remain correlated. Many factors have been proposed as impacting this critical pathway, including the free energy difference between donor and acceptor, the size of the donor and acceptor domains, the existence of triplet states below the charge transfer state, the orientation/packing of molecules at the interface, and even the dielectric constants of the donor and acceptor. However, the relative importance of these various factors is not understood and materials design suffers as a result. For example, attempts to increase cell voltage may inadvertently sacrifice quantum efficiency, and vice versa.

We propose to address these challenges by combining our team’s expertise in the tailored design of both organic and inorganic materials closely with its expertise in device measurement, optical spectroscopy, and nanoscale probes. We will develop new materials to harvest more of the solar spectrum, while at the same time uncover the factors that control relative branching ratios between geminate recombination and free carrier generation at model donor/acceptor interfaces. These studies seek to identify the design rules and fundamental performance limits for new organic and hybrid organic/inorganic photovoltaic materials. Specifically, we propose to (1) develop new p-type polymers with tailored energy level offsets and different morphologies (e.g., nanowires) to systematically explore the effects of energetics and morphology on recombination loss in polymer/fullerene systems; (2) develop 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; (3) design and study new hybrid inorganic quantum dot/polymer combinations for extending the response of solution-processable solar cell materials into the near and mid-IR; (4) manipulate the surface chemistry and facets of ZnO nanostructures towards studies of effects of dielectric constant and morphology on charge injection rate and surface recombination rate in organic/inorganic hybrid systems; and (5) use a suite of experimental tools to probe and quantify the performance limits and loss mechanisms in BHJ solar cells based on various model donor/acceptor pairs produced in this project.

Organic and hybrid organic/inorganic solar cells provide a promising route towards photovoltaic technologies which could be cost competitive with fossil fuels and that could be manufactured on a sufficient scale to impact our energy needs. However, fundamental progress is needed on many fronts before such a vision can be realized. This project will yield new organic and inorganic materials, advance the development of new nanoscale characterization tools, and produce basic new physical insights to underpin the rational advancement of organic and hybrid photovoltaics. Such a project is, by nature, highly interdisciplinary and involves cross-fertilization of molecular and nanoscale science and engineering across three departments (chemical engineering, chemistry, and materials science).

Fundamental Studies of Charge Transfer in Quantum Confined Nanostructure Heterojunctions and Applications to Solar Energy Conversion

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Students:	3 Postdoctoral Fellow(s), 5 Graduate(s), 0 Undergraduate(s)
Funding:	$650,000

We have developed nanomaterials of several materials and nanoscale heterostructures for spectroscopic investigation. We have synthesized single-crystal iron pyrite (FeS_2) nanowires (NWs) with 4-10 nm diameter, via a thermal sulfidation process, and structurally characterized them to be the pyrite phase. Physical property characterization showed the NWs to be semiconducting with heavy p-type doping. Pyrite is an earth-abundant semiconductor promising for solar energy conversion. We have developed an improved method to synthesize hematite (α-Fe_2O_3) NWs via thermal oxidation that reduces reaction time while improving NW density and uniformity. We have also developed a procedure to dope the hematite NWs and significantly improved their conductivity. We have succeeded in synthesizing heterostructures of PbSe QDs with α-Fe_2O_3 NWs by combining the colloidal QD synthesis with the NWs prepared via vapor phase growth. The key is the vacuum surface treatment we developed that ensures the epitaxial integration of the two nanostructures. The results are QD-decorated NW structures with the size of QDs tunable by controlling the temperature of the colloidal synthesis. These nanostructures will be the model systems for the multidimensional spectroscopy investigation.

We have investigated several routes to chemical assembly of PbSe-TiO_2 heterojunctions that are stable in nonpolar solvents using organic linkers and have used time-resolved surface photovoltage (SPV) measurements to characterize how the nature of the ligand impacts the electron transfer efficiency and the stability of the surface ligands. We have set up the TR-SPV measurement using a nanosecond Nd:YAG pulsed laser, a fast amplifier, and a digital oscilloscope to enable measurement of charge transfer and recombination times. Our recent results show that ligands with amino groups are able to stabilize nanoparticles against photo-oxidation by removing the hole from the nanocrystal. Measurements using time-resolved photoluminescence, TR-SPV, and optical absorption show a strong correlation. Finally, we have been developing an ultrafast TR-SPV system using the femtosecond pulsed laser system to measure short recombination or electron transfer lifetimes by exciting a sample with two pulses separated by a time delay and monitoring the SPV signal at different delay times.

We have performed the first multiresonant coherent multidimensional spectra on PbSe quantum dots. Three types of spectroscopy were demonstrated: 2-D frequency/frequency scans that identified coupled spectral excitonic features, 2-D time delay scans that changed the time order of the interactions with the different excitation pulses over all coherence pathways, and 2-D frequency/time delay scans that measured the relaxation rates for different excitions. We demonstrated line-narrowing of the inhomogeneously broadening. We developed simulations that were able to extract the homogeneous and inhomogeneous broadening of the different exciton and biexciton states, the Coulombic coupling of the biexciton, and the relative transition moments for different excitonic states. We demonstrated that these methods were able to directly probe surface states, and we showed that there was ultrafast transfer of the excitonic state directly to the surface state. We have now implemented a femtosecond system that will be able to tune over a much larger range and directly resolve the coherent dynamics.

DOE National Laboratories

Innovative and Complex Metal-Rich Materials

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Funding: $920,000

This project works to (1) uncover and ultimately design new families of intermetallic phases and to understand the factors that stabilize both new and known phases by combining experiment, viz. exploratory synthesis, temperature-dependent structure determinations, and surface characterizations, with electronic structure theory; (2) examine the fundamental surface characteristics of complex intermetallics by investigating fundamental issues in surface science related to complex metal-rich solids in bulk phases; and (3) establish structure-property relationships for complex metal-rich materials in the bulk and at their surfaces as related to both practical as well as fundamental issues, e.g., thermoelectric, magnetocaloric, catalytic, tribological, and structural 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.

Solid State NMR of Heterogeneous Polymer Systems

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Funding: $725,000

Advanced solid-state nuclear magnetic resonance (NMR) methods are developed and applied for elucidating the nanometer-scale structure and dynamics of complex materials under the following types of conditions: Ionomers as used, for instance, in all-solid H_2/O_2 fuel cells; Biological and biomimetic nanocomposites; Complex tellurides for thermoelectric and other applications. For instance, a definitive new model of the nanometer-scale structure of the Nafion ionomer, the benchmark material for fuel-cell proton-exchange membranes, has been established based on high-resolution ^{13}C and ^{19}F NMR and quantitative scattering analysis. ^{1}H-^{31}P/^{29}Si/^{13}C NMR methods for proving nanocomposite formation and measuring the thickness of inorganic nanocrystals in an organic matrix, for instance in bone and bone-mimetic materials, have been introduced. Recently, high-resolution, magic-angle-spinning ^{125}Te NMR was introduced as a new tool for characterizing the composition, as well as the charge-carrier concentration and its distribution in high-performance thermoelectrics.

Directed Energy Interactions with Surfaces

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Funding:	$520,000

The Directed Energy Interactions with Surfaces Program focuses on fundamental studies of the interaction of directed energy sources such as energetic ions, electrons, and photons with materials. These interactions provide the basis for characterizing, modifying, patterning, and analyzing materials. The fundamental understanding of energy-material interactions drives the development of world-class instruments and methods for materials characterization, which in turn enables us to answer questions about new or previously unobservable phenomena and develop new materials.

The long-term goal of the fundamental studies is to understand the interaction of directed energy sources with materials, both in model systems, in which basic interactions can be studied in great detail, and in complex systems, in which multiple interactions occur and evolve over varying length and time scales.

The long-term goal of the instrument development program is to create instruments with unique capabilities in high-precision ultra-trace and nanoscale elemental, molecular, and isotopic analysis. We are developing a multidimensional approach in which most or all observables of energy-material interactions are detected simultaneously and correlated with each other to give a complete description of the energy-material interaction.

Fundamental Studies of Electrocatalysis for Low Temperature Fuel Cell Cathodes

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Students:	4 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,160,000

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.

Nanostructured Thin Films

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Students:	3 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$825,000

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 to 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.

Rational Synthesis of Superconductors

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Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $750,000

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 (a) density-wave instabilities (spin and charge), and their suppression through chemical doping in order to generate superconductivity that may emerge from phase competition, and (b) how narrow energy band gaps and facile doping properties could lead to a superconducting state. In the former we investigate low-dimensional intermetallics exhibiting magnetic interactions and spin density waves. In the latter we investigate narrow band ternary and quaternary chalcogenide phases comprising heavy elements such as lead, bismuth, selenium and tellurium. We use a conceptually robust tool in designing, predicting and creating sequences of structurally related materials. The project focuses on relationships between structure, composition, electronic structure and physical properties. In the long term, we expect to clarify the influence of various building blocks on the physical properties and enhance our ability to further design members exhibiting superconductivity.

Chemical and Mechanical Properties of Surfaces, Interfaces and Nanostructures

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Yang, Peidong, LAWRENCE BERKELEY NATIONAL LAB
Students: 4 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding: $1,460,000

The purpose of this program is to carry out atomic level studies of surfaces and nanomaterials, focusing on chemical, mechanical and physical properties such as 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 benefits 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 such as 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).

The Chemical and Mechanical Properties of Surfaces, Interfaces and Nanostructures program additionally received at least half of the research effort of one postdoctoral fellow who was supported by an outside source (fellowship, TAship, etc).

Inorganic/Organic Nanocomposites

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Wang, Lin-Wang, LAWRENCE BERKELEY NATIONAL LAB
Yang, Peidong, LAWRENCE BERKELEY NATIONAL LAB
Students: 4 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding: $1,253,000

This activity is directed towards organic/inorganic nanocomposite materials. The goal is 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.

Nuclear Magnetic Resonance

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Sr. Investigator(s):
Students: 3 Postdoctoral Fellow(s), 5 Graduate(s), 0 Undergraduate(s)
Funding: $1,000,000

The nuclear magnetic resonance (NMR) program has two complementary components. The first is the establishment of new concepts and techniques in NMR and its offspring, magnetic resonance imaging (MRI), in order to extend their applicability and enhance their capability to investigate molecular structure and organization from materials to organisms. The study and diagnostic use of nuclear spins interacting with each other and with others degrees of freedom requires the development of new theoretical and experimental methods; one consequence of these efforts is the design and fabrication of next-generation NMR and MRI equipment. The second component of the research program involves the application of such novel methods, together with other programs, and with outside laboratories and industry, to significant problems in chemistry, materials science, and biomedicine. It is the unique environment of interdisciplinary research and large-scale instrumentation capabilities at the Lawrence Berkeley National Laboratory that cultivates these innovations, their diverse applications, and technology transfer.

The Nuclear Magnetic Resonance program additionally received at least half of the research effort of one postdoctoral fellow and six graduate students who were supported by outside sources (fellowship, TAship, etc).

Physical Chemistry of Inorganic Nanostructures

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Students:	2 Postdoctoral Fellow(s), 6 Graduate(s), 0 Undergraduate(s)
Funding:	$1,646,000

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.

The Physical Chemistry of Inorganic Nanostructures program additionally received at least half of the research effort of three postdoctoral fellows who were supported by outside sources (fellowship, TAship, etc).

Plastic Electronics

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Students:	1 Postdoctoral Fellow(s), 5 Graduate(s), 0 Undergraduate(s)
Funding:	$1,000,000

This program is aimed at studying the fundamental molecular and physical principles that govern the design of materials for organic and plastic electronics. Design, synthesis and characterization of new molecules and polymers will allow us to explore materials with new functional properties. Comparison of these properties through device characterization and photophysical experimentation will allow us to determine structure-property relationships and general design rules for optimized organic electronic materials for energy-related technologies.

Giant Nanocrystal Quantum Dots. Controlling Charge Recombination Processes for High-Efficiency Solid-State Lighting

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Students:	3 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$651,000

Multiple technical challenges stand in the way of achieving robust, high-efficiency solid-state lighting (SSL). These were summarized in the report of the DOE-BES Workshop on SSL (2006) in terms of two Science Grand Challenges: (1) the need to develop the fundamental understanding of light-emitting materials and nanostructures toward rationally designed SSL structures from the ground up and (2) the need to control the competing pathways by which electricity is converted into light. Here, we directly address both of these Science Grand Challenges. We establish the fundamental knowledge necessary to develop a new class of emitting nanostructures that will serve as high-efficiency, robust "building blocks" for rationally designed SSL. Further, we base this transformative development on a novel type of semiconductor nanocrystal quantum dot (NQD) – the so-called "giant" NQD (g-NQD) – that affords unprecedented control over excitation-to-photon conversion processes. Our research is organized around three interrelated Research Goals that deal with fundamental aspects of g-NQD chemistry and photophysics toward a proof-of-principle device demonstration. These Research Goals are summarized as to (1) understand the precise relationships between g-NQD structure and optical performance toward controlling critical aspects of structure that otherwise lead to non-uniformity in function, (2) understand the intrinsic and extrinsic g-NQD properties that control carrier recombination processes and eliminate losses in the light-emission process by manipulating these properties, and (3) demonstrate that the unique g-NQD chemical and photophysical properties translate into significantly improved NQD-LED performance. We envision that this work will build practical foundations for realizing robust, reduced-cost, high-efficiency SSL technologies.

Hydroxide Conducting Systems Fuel Cells

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Sr. Investigator(s):	
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Funding:	$130,000

The primary advantage of an alkaline system for fuel cells is the enablement of non-precious metal catalysis, a critical showstopper to widespread implementation of traditional (acidic) fuel cells. Alkaline systems have been largely ignored by the fuel cell community due to concerns with carbonate formation and the inability to produce anion exchange membranes (AEMs) of acceptable stability at high pH. Much of what appears in the literature suggests that AEMs have inherent durability limitations, significantly limiting operating times and temperatures in devices. To date, our experimental studies of cation durability suggest greater durability than what has been reported for AEMs providing hope that increased durability membranes can be developed. These statements highlight the lack of understanding of cation degradation and the impact of covalently tethering cations in polymers. In order to try to fill this gap, we have used chemical and thermal degradation studies to elucidate the degradation mechanisms and rates of target cations and correlated these studies with computational studies. These studies have shown the importance of ylide formation as a degradation pathway beyond SN2 attack, the role of water (solvating media) in stabilizing cations, and explored cations with increased stability. The results of the work provide a greater understanding of the fundamental aspects of hydroxide conductors for fuel cell and electrolysis applications, and will be applied to our future work which continues the search for the next generation of AEMs.

Hydroxide Conducting Systems Fuel Cells

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Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$270,000

The purpose of this work is to provide a fundamental understanding of the stability and performance of hydroxide and/or carbonate conducting materials, and from this understanding, develop novel materials to help enable a hydrogen-based economy. The primary advantage of hydroxide conductors is the enablement of non-precious metal catalysis, a critical showstopper to widespread implementation of traditional (acidic) fuel cells. We have used chemical and thermal degradation studies of target cations for use in anion exchange membranes (AEMs) to elucidate the degradation mechanisms and rates of target cations and correlated these studies with computational studies. These studies have shown the importance of ylide formation as a degradation pathway, the role of water (solvating media) in stabilizing cations, and explored cations with increased stability. Recently, advances in AEM durability have been reported that are in reasonable agreement with our experimental 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. Issues involving carbonate formation and performance have not been adequately addressed or demonstrated. Our continuing work will focus more strongly on the fundamental role of carbonate and bicarbonate in these systems as these species will be present whenever carbon dioxide is present and appear to be a potential limiting factor in implementing AEM fuel cells. These studies will help lead to improved materials and commercializable, Pt-free fuel cells.

Materials and Interfacial Chemistry for Next Generation Electrical Energy Storage

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Students:	3 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$800,000

Electrochemical energy storage systems (EES), specifically batteries, are critically needed for effectively using clean, abundant renewable sources of energy and effectively integrating these sources into the electrical grid. Furthermore, the development of electric vehicles (EVs) 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 the 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) the understanding and controlling processes that occur at the anode, (2) the understanding and controlling mechanisms that occur at the cathode, (3) the understanding voltage limits imposed by the electrolyte, and (4) the design of new inorganic or polymer/ceramic composite electrolytes that allow the use of alternative, high capacity cathodes. Thus, this proposal addresses opportunities for transformative advances in batteries for vehicle and stationary storage applications.

This FWP is partnered with a university project led by John Goodenough (University of Texas, Austin). The focus of the ORNL research effort lies in characterization and electrolytes.

Polymer-Based Multicomponent Materials

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Funding: $2,038,000

The central goal of this research is to develop a fundamental understanding of the 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; 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 function 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, as well as a wide range of theoretical tools.

Solid State NMR Characterization of Ultra Capacitor Materials for UT Austin

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Funding: $47,000

This research effort is part of the SISGR-EES Program lead by Rod Ruoff, University of Texas at Austin. The broad objective of the SISGR program is to advance the fundamental scientific understanding of electrochemical double layer capacitance (EDLC) and thus of ultracapacitor systems composed of a new type of electrode based on chemically modified graphene (CMG) and (primarily) with ionic liquids (ILs) as the electrolyte. The objective of the Sandia component for this project is to provide both solid state NMR characterization of these materials and interfaces, along with implementation of pulse-field-gradient (PFG) NMR to directly measure diffusion rates of the IL in electrolyte solutions.

During the 2011 fiscal year Sandia has continued to provide NMR characterization of the unique tetra-alkyl ammonium ionic liquids (IL) being developed and tested by the Bielawski group (UT Austin), as well as the graphene nanocomposites developed by Ruoff group (UT Austin). This NMR effort has resulted in two published manuscripts in 2011, including one describing the development of NMR theory to obtain molecular correlation times directly from 14N NMR relaxation experiments, without resorting to motional-regime assumptions (Alam, 2011). In the upcoming year our efforts will be directed towards the combination of pulse field gradient (PFG) NMR experiments measuring self-diffusion constants as a function of temperature and the results of the 14N NMR relaxation experiments. These experiments are expected to provide additional fundamental understanding of the molecular associations (ion-pairing and clustering) in IL electrolytes. These NMR experiments are also being extended to probe the surface interaction of IL with graphene and graphene oxide. In addition, we have also begun development of solid state 14N MAS NMR experiments to look at the molecular dynamics and local interactions in solid IL. These classes of IL, which are solid at room temperature, have recently been shown by the Bielawski group to demonstrate increased capacitor performance.

Diamondoid Science and Applications

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Funding:	$792,000

Diamondoids are unique new carbon-based nanomaterials consisting of 1-2 nanometer, fully hydrogen-terminated diamond particles. Unlike their conjugated counterparts, graphene or carbon nanotubes, the carbon atoms in diamondoids are sp3 hybridized, leading to unique electronic and mechanical properties. Diamondoids behave much like small molecules, with atomic-level uniformity, flexible chemical functionalization, and systematic series of sizes, shapes and chiralities. At the same time diamondoids offer more mechanical and chemical stability than small molecules, and vastly superior size and shape control compared to inorganic nanoparticles. This family of new carbon nanomaterials is thus an ideal platform for approaching the Grand Challanges of energy flow at the nanoscale and synthesis of atomically perfect new forms of matter with better precision than any other nanomaterials system.

This program explores and develops diamondoids as a new class of functional nanomaterials based upon their unique electronic, mechanical, and structural properties. This includes all phases of 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, theory, and thin film growth. This naturally requires the broad expertise and collaboration between a number of investigators to successfully craft an approach to 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.

Mechanical Behavior and Radiation Effects

Institutions Receiving Grants

The Inverse Magnetoplastic Effect of Magnetic Shape-Memory Alloys

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Funding:	$144,000

We study fatigue mechanisms of magnetic shape-memory alloys and methods to improve the fatigue life. For this purpose, we apply coatings to Ni-Mn-Ga single crystals. The coatings provide pinning sites for twinning dislocations that prevent long-range motion of twin boundaries. A nonlinear strain behavior of the coatings prefers uniform straining of the MSM sample to local straining. A dense twin structure with thin twins results in uniform straining. In contrast, a coarse twin structure leads to more local straining. A dense twin structure prevents the formation of orthogonal twins. Orthogonal twins form frequently in coarse twin structures. The interaction of orthogonal twins causes crack nucleation in cyclic applications and leads to fracture. Hence, stabilization of the dense twin structure increases the fatigue life of MSM materials.

We selected $Ni_{51.3}Mn_{26.3}Ga_{22.4}$ (in at %) as a test material. An MSM sample of about 1 x 2 x 20 mm^3 was coated with titanium nitride of 1 micrometer in thickness on three long sides of the sample. Initially, the sample exhibited a two-variant structure and it strained about 6 % in a magnetic field of a sufficient strength. Twins in the uncoated sample were very broad. In one variant, the short crystal axis c is parallel to the long dimension of the sample, and in the other variant, the c axis is perpendicular to the sample surface. After coating the sample on three surfaces, the sample exhibited a multivariant twin structure due to high coating temperature and constraining effects of the coating. After turning the magnetic field of 1 Tesla between the directions of the long dimension and short direction for several times, a two-variant twin structure was recovered. The twins were very thin. The average width of twins was only about 20 µm. The twins remained thin also after straining the sample hundreds of times by a magnetic field and by a mechanical stress. The sample strained about 2.5 % in the magnetic field. Twinning stress was increased after coating. After removing the coating by grinding and electropolishing, the initial broad twin structure recovered.

An MSM sample of about the same composition and size was cast in an elastomeric resin. The sample remained martensitic during curing due to the low curing temperature of the resin. The sample exhibited broad twins initially. After encasing in resin, the twins were thin and regularly spaced. They remained thin also after straining of the sample by the magnetic field and the mechanical stress. The width of the twins was about 100 µm. When the elastomeric resin was removed, the initial coarse twin structure recovered.

The theory of deformation twinning making use of twinning disconnections is well-established in the field of crystal plasticity. This theory has found little attention in the MSMA community. Neglecting the basic principles of twin crystallography has hindered a fundamental advancement towards understanding the effects of microstructure and martensite crystallography on the magneto-mechanical properties and, particularly, on inverse magnetoplasticity of the MSMA Ni-Mn-Ga. This part of the project aims at rigorously applying the crystallographic theory of twinning and twinning disconnections to the various martensite structures and twinning systems of Ni-Mn-Ga.

The ground state of the martensitic phase with composition near Ni_2MnGa is thought to be tetragonal. However, several studies have reported modulated forms with monoclinic symmetry, such as 14M, due to the intrusion of nano-scale twinning. Using TEM imaging, we found that this microstructure results from deformation twinning produced by motion of disconnections with Burgers vector $\mathbf{b} = 1/6[100]$ and step height $h = d_{(002)}$ on the (001) twin plane, where the indexing is referred to the "monoclinic" 2M structure. Kinematical theory was also used to confirm our experimental observation that diffraction patterns vary from being characteristic of the 2M structure at one extreme to the 14M structure at the other extreme, depending on the extent and spatial configuration of the twinning. The origin and extent of twinning was addressed using the topological theory of martensitic transformations. We found that (001) twinning is the lattice-invariant mode of deformation necessary to accommodate one component of the misfit at the austenite-martensite interface. The other component is accommodated by an array of disconnections whose motion across the interface also produces the transformation.

An important finding is the coincidence of the $60\text{-}2_{(2M)}$ and $600_{(2MT)}$ reflections. This implies that the twinning shear is $a/3d_{(001)}$, which is about 1/3. Micrographs of twin tips indicate three levels of contrast, consistent with elementary twinning disconnections with $\mathbf{b} = 1/6[100]$ and $h = d_{(002)}$. When the operative reflection was $\mathbf{g} = 200_{(2M)}$, the phase shifts produced by a train of six elementary twinning disconnections was $2\pi * \mathbf{g} * n\mathbf{b}$, i.e., $2\pi * (1/3, 2/3, 1, 1/3, 2/3, 1)$.

Understanding and Controlling Toughening Mechanisms in Nanotube Reinforced Ceramic Coatings

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Funding: $220,000

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 research at Brown University that has provided the first direct evidence that ceramics can be toughened with multiwalled carbon nanotubes (MWNTs). The research conducted in this BES program focuses primarily on developing fundamental understanding of toughening mechanisms. These investigations consist of well-integrated experimental and theoretical/computational efforts. The experiments are investigating ceramic coatings reinforced with nanotubes, to obtain detailed information on the relationships between materials characteristics and mechanical behavior. The modeling efforts are based on integrating atomistic, mesoscale, and continuum descriptions. These are aimed at an understanding of deformation and interfacial sliding on the nanoscale, and on correlating nanoscale material properties with behavior at larger length scales. These combined efforts will identify how features of the material, at atomistic and microstructural scales, lead to macroscopic properties. These efforts will ultimately be used to guide the design and synthesis of new nanoceramic composite materials.

Investigation of Radiation Damage Tolerance in Interface-Containing Metallic Nano Structures

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Funding:	$150,000

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. The attention will be focused on studying the following interfaces (likely) in order of increasing affinity for vacancy absorption: grain boundaries in a monolithic bcc metal, bcc/fcc and bcc/bcc interfaces, and periodically arranged metallic glass/metal multi-layers spanning the entire nano-pillar volume. The model material systems are (1) pure Fe containing 1-5 grain boundaries, (2) a single Fe (bcc)-Cu (fcc) boundary per pillar oriented perpendicular to the pillar axes, (3) a single Fe (bcc)–Cr (bcc) boundary per pillar oriented perpendicular to the pillar axes, and (4) periodically arranged CuxZry metallic glass/Cu nanolaminates with thicknesses between 15nm and 100nm. A FIB-less nano-pillar fabrication approach with precise initial microstructure control (both dislocation density and grain boundaries) and experimentally determined stress-strain relationships will be enhanced by in-situ SEM observations coupled with TEM microstructural characterization of the same samples before and after deformation and atomistic modeling. The PI will conduct a comprehensive suite of experiments to quantitatively assess the key parameters for He bubble nucleation and growth by independently varying the sink strength, sink proximity, and implantation temperature. Pillars containing He-enriched interfaces will be tested under uniaxial tension to assess embrittlement, resulting boundary strength, and deformation mechanisms. Successful execution of this work will help identify which types of interfaces are particularly resilient against radiation damage.

Energetics of Radiation Tolerant Nanoceramics

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Funding:	$150,000

Nanostructured materials are likely to play a large role in future nuclear reactors and radioactive waste storage due to their strength and potential resistance to structural damage from radiation. However, this potential is hindered by significant gaps in the understanding of interfaces' properties and their role in the overall performance of the nanocrystalline structures. The lack of reliable thermodynamical data of nanomaterials makes it extremely difficult to predict and fully exploit nanomaterials' properties in high-radiation environments, this being one of the major reasons why the stability of the nanomaterials is still a big unresolved question.

The goal of this project is to investigate nanomaterials with potential interest for nuclear components [the aluminate based spinels (MAl_2O_4, M = Mg, Ni, or Zn), investigate zirconia based materials (ZrO_2 doped with Mg, Y, or Ca), and establish the link between composition, interface thermodynamics, and radiation resistance, aiming to enable a better understanding of the nature of enhanced performance in nanocrystalline ceramics. Thereafter, we will exploit the achieved knowledge as a foundation in order to design a new nanocomposite ceramic capable of withstanding high radiation exposition by using elements of interface engineering on a thermodynamic basis.

Mechanical Behavior in Ceramics with Unusual Thermal-Mechanical Properties

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Funding:	$120,000

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. Part of the work during the next period of funding will be to survey potential ceramics and perform preliminary experiments in the context of what is learned through the more extensive studies with eucryptite.

The Coupling Between Interfacial Charge and Mechanical Deformation at High Temperatures in Ceramics

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Funding:	$150,000

The overall scope of this research effort is to understand how applied electrical fields interact with stress–induced interfacial thermodynamic and kinetics in ceramics at high temperature. The experimental approach is to investigate how electrical fields applied to oxide ceramics with a pair of electrodes influence densification and deformation at high temperatures. Sinterforging experiments where densification and shear deformation are achieved simultaneously are typical of this approach. One of the most intriguing results from this project has been the discovery of an unusual effect: that yttria stabilized zirconia can be sintered and superplastically deformed in just a few seconds at furnace temperatures well below 1000 °C under DC fields applied by means of a pair of electrodes directly to the specimen. We have called this phenomenon flash-sintering and flash-sinterforging. This effect occurs at a threshold combination of electric field and furnace temperature: a higher field lowers the onset of flash-sinterforging. A further unexpected result is that both the applied stress and the electrical field reduce the temperature for the onset of the flash effect, the implication being that applied stress and the temperature act in equivalent ways. The flash phenomenon has another characteristic: the onset of densification is accompanied by a sudden increase in the electrical conductivity of the oxide ceramic. However, the Joule heating induced by high conductivity does not raise the temperature to explain sintering and deformation in a few seconds. These findings raise a clear fundamental question: what is the mechanism whereby both mass transport, required for sintering and diffusional creep, and electrical conductivity, which is controlled by the faster moving charged species, are coupled. The proposed hypothesis being investigated is that the flash-effect is precipitated by a defect avalanche that causes both an increase in the mass transport and electrical conductivity. The nucleation of Frenkel pairs followed by ionization of the charge on interstitials and vacancies by the Poole-Frenkel mechanism is being investigated. The role of applied stress is being studied in terms of a newly defined electro-chemo-mechanical potential.

Continuum Plasticity: From Grain Boundaries and Coarsening to Cellular Structures and Recrystallization

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Funding:	$250,000

Under external load, crystals may plastically deform or undergo fracture. Under plastic deformation, dislocations tangle and organize into complex structures, often forming cells nearly free of dislocations separated by fairly sharp walls. The mechanical behavior of practical materials (yield stress, work hardening, transport) in single-phase materials is typically dominated by these emergent structures. Our group has been exploring a continuum dislocation dynamics model that spontaneously generates these cellular structures. As in some experiments, these structures are fractal, with self-similar scale-invariant features. As in other experiments, these structures get smaller (refine) and have larger misorientations as the crystal is deformed. We have been studying this behavior using correlation functions of dislocation density, plastic deformation, and crystalline misorientations, and find that they exhibit scaling behavior consistent with one underlying critical exponent. Exploring three different models in fully three-dimensional simulations (one allowing climb and two methods of restricting to glide-only dynamics), we find remarkably similar structures and scaling exponents. We are incorporating vacancy diffusion into our models, attempting to adapt them to study polycrystalline coarsening, and (separately) studying the self-similar temporal features of dislocation dynamics—crackling noise observed most recently in micropillar and nanopillar compression tests.

One of the key analytical methods in fracture is the use of extreme value statistics to understand the fracture stress distribution in engineering failure studies. The Weibull distribution (one of three universal limiting forms) is named for the fracture engineer who originated it. It is entertaining to note that extreme value statistics is a simple example of a renormalization-group fixed point: the theory developed to study continuous transitions is applicable to the prototype of abrupt events. To our surprise, in a collaboration studying the role of interactions between cracks in a fuse-network model, we found a failure distribution that was not described by a Weibull law. Instead, a simple distribution analogous to critical droplet theory accurately described the failure distribution. (We can show in principle that this droplet theory eventually converges to a Gumbel distribution, but only for samples of astronomical size.) So both the renormalization-group tools used for continuous transitions and the critical-droplet tools used for abrupt thermodynamic transitions are applicable to fracture. We conclude that Weibull distributions are not always reliable in extrapolating to rare events, and that much more effective (but less universal) estimates can be made given some understanding of the underlying failure mechanism.

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

The ultimate goals of this multiyear project are (1) the creation of a new quantitative understanding of fatigue damage accumulation and microcrack initiation processes in metallic polycrystals; (2) the creation of a new generation of cyclic deformation-based experimental capabilities at an important DOE facility, the Advanced Photon Source; and (3) the development of next generation simulation tools capable of replicating cyclic experimental loading conditions on virtual polycrystals to enable the interpretation of experimentally observed responses.

Fatigue continues to be one of the most challenging failure modes facing designers of metallic components subjected to repeated loads. While a general understanding exists of the manner in which fatigue cracks initiate from sites of concentrated damage, such as persistent slip bands in ductile metals, an overarching theory capable of predicting the nucleation of a fatigue crack has not emerged. It is qualitatively known that alloys which exhibit strain localization have lower resistance to crack initiation, but no detailed model exists that can account for this propensity in a fundamental way. From an intellectual perspective, developing a comprehensive understanding of the microcrack initiation process associated with cyclic micro-plasticity easily ranks as one of materials engineering's "Grand Challanges." Attacking this problem requires the means to measure grain and subgrain loading conditions and loading-induced damage evolution as well as the modeling capability that accurately captures elastic and plastic behaviors at the grain scale. Typical cyclic plasticity and fatigue research has relied on post-mortem Transmission Electron Microscopy (TEM) studies and fractographs to hypothesize the microcrack initiation process by qualitatively connecting damage to cracking. Fatigue crack initiation is stochastic in the sense that cracks initiate at the "weakest link" in the stressed volume. TEM studies are excellent for characterizing the average damage state but cannot readily reveal the region of most severe damage (the weakest link). High energy x-rays are capable of interrogating large volumes of material during loading in short amounts of time. This creates an immediate advantage in studying fatigue. Fatigue-life models continue to be dominated by empiricism, with very little quantitative connection to actual physical processes associated with fatigue crack initiation. Detailed crystal-based simulations involving more than a handful of individual crystals or for more than a few hundred loading cycles of elastic-plastic deformation behavior have also only recently become feasible.

To develop a new comprehensive understanding of microcrack initiation, we will employ some of the newest diffraction-based micromechanical characterization experiments that currently exist. We also will develop capabilities that currently do not exist. In the process, we will work to lower the barriers to the use of diffraction based experiments in addressing real problems in materials science and engineering, moving the scientific discovery from the x-ray science to the improved understanding of materials. For interpretation of the experiments, we will advance the state-of-the-art for instantiating high fidelity virtual polycrystals, for simulating cyclic loading histories applied to the virtual polycrystals, and for extracting distributions of lattice strains and defects in the microstructure that are entirely consistent with the diffraction patterns. Our research team, which has expertise in diffraction, mechanical testing, computational methods, and metallurgy is ideal for the task at hand. The proposed research is decomposed into three phases for a total of 10 years. Each phase has a distinct set of objectives and deliverables but each will build off the accomplishments of its predecessor. The strong experiment development mission of the project ensures that new capabilities developed during one phase will become available to the mechanics of materials research community at APS in the following phase.

Structure/Property Relationships in High Strength Nanostructured Spinodal FeNiMnAl Alloys

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Funding:	$150,000

The aim of this project is to understand the deformation mechanisms that control the strength of recently-discovered, potentially-useful, two-phase B2/L2$_1$ FeNiMnAl alloys. These alloys, which form via spinodal decomposition, are nanostructured (wavelength of 8-10 nm) and have high room-temperature yield strengths of ~1450 MPa. The work focuses on one of these alloys ($Fe_{30}Ni_{20}Mn_{20}Al_{30}$) that is being aged to produce different microstructures and mechanically tested over a range of temperatures and strain rates. 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 are producing three different microstructures in $Fe_{30}Ni_{20}Mn_{20}Al_{30}$: (1) the ultrafine, as-cast spinodally-formed modulated B2/L2$_1$ microstructure; (2) a microstructure consisting of fine <100>-aligned L2$_1$ particles in a B2 matrix, produced by aging the cast alloy at low temperature; and (3) a microstructure consisting of larger, possibly globular, L2$_1$ particles in a B2 matrix, produced by aging at higher temperature.

Second, we are characterizing the resulting microstructures. Some specific questions that we will attempt to answer are: Do the phases lose coherency upon aging as the size of the particles increases? How does the matrix/particle interface dislocation structure depend on the particle size? How does the degree of order of the two phases vary with temperature? Do the compositions of the particles and matrix change significantly with temperature?

Third, we are determining how the strength depends on both temperature and strain rate for each of the three different microstructures.

Fourth, we are determining the deformation mechanisms for a variety of temperatures and strain rates for the three 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. We are also determining the matrix-particle dislocation interactions (i.e., does dislocation cut through the particles, loop around them, glide along channels between the particles, or, at high temperatures, climb over them?).

Coupling these observations to the microstructure and mechanical properties will enable us to model the mechanical behavior.

Statistical Mechanics Modeling of Mesoscale Deformation in Metals

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Funding:	$108,000

The objective of the proposed research is to conduct first principles based theoretical and computational investigation of dislocation patterning and strain hardening during plastic deformation of single crystal FCC metals. By replacing the top-down constitutive laws of continuum plasticity with kinetic equations within a density-based model of dislocation dynamics, which is developed based on the principles of statistical mechanics, the theory of discrete dislocations will be bridged to the theory of crystal mechanics. The solution of the kinetic equations, in conjunction with crystal mechanics, will then provide the space-time evolution of the dislocation density as well as the rate of plastic slip on various slip systems from the dislocation flux. The dislocation kinetic equations explicitly account for the fundamental physics of dislocation glide, cross slip, and short-range interactions. The dislocation correlations required to close the kinetic equations governing the dislocation density evolution will be extracted by statistical analysis applied to dislocation dynamics simulation data obtained using dislocation dynamics simulation. A robust finite element scheme will be used to solve the coupled equations of dislocation kinetics and crystal mechanics, which will make it possible for the first time to predict the deformation-induced space and time evolution of the dislocation densities (patterning), plastic strain distributions, and the internal stress and crystal distortion fields. Mesoscale dislocation patterning and strain hardening simulations will be performed for Al and Cu single crystals under monotonic (tensile and compression) loading and compared with existing deformation data from open literature, and with the more recent submicron resolution 3D synchrotron-based x-ray microscopy measurements of mesoscale deformation fields in single crystals. The theoretical foundation of the proposed approach has mostly been established, and the primary focus of the proposed project will be on the implementation.

This proposal tackles the metal deformation problem, one of the oldest and costly issues in metal research, by embedding a statistical-mechanics-based kinetic formalism of dislocations into the crystal mechanics framework to replace the phenomenological constitutive laws. This approach will thus lead to the genesis of a new predictive physical theory of crystal plasticity and open entirely new avenues for modeling crystal deformation and for understanding of dislocation patterning, work hardening, recovery, and strain localization in crystals in a unified fashion.

NanoMechanics: Elasticity and Friction in Nano-Objects

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Funding:	$140,000

Our research program is focused on the study of the frictional and elastic properties of nano-objects, such as carbon nanotubes, nanowires, nanosheets, and piezoelectric and photostrictive nanostructures, simultaneously with the morphological, structural, and chemical properties of individual nano-objects. 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.

The research activity is focused on three areas:

(1) Friction and frictional anisotropy in carbon nanotubes as a function of their chirality, electrical properties, and defects. Friction and adhesion forces between individual nano-objects, such as a nanoparticle or a nanotube, and a plain or patterned substrate as a function of size, structure, and surface chemistry.

(2) Elastic properties of oxides nanowires and nanosheets as a function of their size, structure, defects, and temperature.

(3) Piezoelectricity, exoelectricity, photostiction, shape memory, and pseudoelasticity in nanowires produced by a method (thermochemical nanolithography) recently developed by the PI. The focus is on the role of size, geometry, and defects.

Materials for Extreme Irradiation Environments

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Funding:	$650,000

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 has been, however, that these materials are not typically stable under irradiation and are thus limited in their overall viability for general application. In this cluster, we are exploring a novel approach to overcome this problem by investigating nanostructures that are induced by the irradiation itself and are thus stable by design. By alloying an elemental matrix with one or several solute elements, we have begun to gain control of the phase stability of these nanostructures and can now explore how to improve their 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.

We are continuing our the study of Cu-base model alloy systems, as the wide range of solute miscibility and diffusivity in Cu affords great flexibility in controlling driving forces and kinetics of nanoprecipitation under irradiation. Systematic studies in Cu-Fe and Cu-V alloys have confirmed that in these moderately immiscible systems, stationary nanostructured states can be achieved by irradiation. Furthermore, using atom probe tomography, a novel precipitation morphology has been identified in these irradiated Cu-Fe and Cu-V alloys, where solute-rich precipitates enclose Cu-rich inner precipitates, resulting in a "cherry-pit" structure. This novel morphology, which we also observed in atomistic computer simulations, is a clear signature of the nonequilibrium character of the nanostructuring induced by irradiation. This research has been extended to other base materials, such as Ni-base, and to ternary alloy systems, such as Cu-W-Nb. These extensions augment greatly the range of nanostructures that can be stabilized by irradiation, thus affording greater flexibility in selecting nanostructures with optimized properties. A new research effort has been also initiated to quantify the spatial distribution of solutes and second phases relative to relevant microstructural features such as dislocations and interfaces. To achieve this goal, we are using primarily transmission electron microscopy (TEM) based imaging, spectroscopy, and tomography, and we have designed and constructed a special sample holder to enable atom probe tomography analysis on the same samples.

In conjunction with microstructural characterization, we are investigating the mechanical properties of model nanostructures, with an emphasis on developing techniques allowing for in-situ measurements. Of particular importance is the creep resistance of these materials, owing to their small grain size. To address this issue, we have modified a bulge test technique on free standing thin films to measure creep in nanograined and nanostructured Cu-W during irradiation at elevated temperatures. Additional nanoscale mechanical testing is being developed, making it possible to test samples carved out from bulk materials.

A modeling effort is developed in conjunction with the above experimental effort. We have employed atomistic simulations to study radiation-induced creep (RIC) in nanograined materials. Initial results reveal a new mechanism of RIC in irradiated nano-crystalline materials, based on point defect relaxations in grain boundaries. Furthermore, development of radiation-resistant structural materials requires the understanding of transport mechanisms of point defects, their coupling to solute atoms, and their interaction with sinks (e.g., dislocations). Point defect transport can be biased by the local stress originating from sinks as well as by applied stress, as in the case of creep. The effect of stress on point defect transport is, however, poorly understood, especially for interstitial defects. As these effects are very sensitive to the specifics of a given alloy system, we are combining ab initio calculations of defect formation and migration energies with continuum transport theory. As a first model system, we have chosen dilute Ni-Si alloys, for which extensive experimental data on radiation-induced segregation and precipitation is available. A collaboration with Dr. M. Nastar (CEA-Saclay, France) has been initiated to develop mesoscale simulations that capture these kinetic coupling effects.

Stress-Coupled Grain Boundary Migration

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Funding:	$137,000

Having shown that stress-assisted room temperature grain growth in nanocrystalline metals is directly related to the coupling of applied shear stresses to a general population of grain boundaries, we are expanding our use of micro-tensile experiments to incorporate the identification of individual grains and grain boundaries with in situ: SEM-based orientation imaging microscopy (OIM), high-energy synchrotron x-ray diffraction, and TEM-based automatic orientation mapping. Coupled with direct observations of boundary motion, these in situ measurements provide a detailed description of stress-assisted grain boundary migration.

Motivated by the desire to conduct in situ experiments, we have recently spearheaded the development of experiments that will combine in situ SEM-based and TEM-based mechanical testing with orientation mapping. Vacuum requirements and limited volumes make an electron microscope a challenging environment in which to conduct tensile tests. We have designed and built an SEM-based in situ tensile stage in collaboration with Schuster at ARL and are studying ultra fine-grained metallic films with the new stage. Resolution limits of SEM-based EBSD will not allow for orientation mapping of nanocrystalline specimens with grain sizes of significantly less than 100 nm, but the newly available NanoMEGAS ASTAR system provides automated orientation imaging and mapping in the TEM. In ongoing collaborations with Legros at CEMES-CNRS, we have designed and fabricated nanocrystalline thin film samples that are compatible with TEM straining grids. These thin film specimens, which are prepared in the Hopkins clean room, are fabricated and shaped on photoresist and then transferred to TEM straining frames. Preliminary results on nanocrystalline Al thin films using the NanoMEGAS ASTAR system at CEMES have revealed the following. The shape of the GB did not appear to inhibit motion. Observations that the largest grains have no orientation preference suggest that coupled grain boundary migration is not driven by surface energy or sensitive to grain orientation. Moreover, observations that mobile GB's were generally high-angle grain boundaries and were not of pure twist character support molecular dynamics simulations of stress-assisted grain growth. Subsequent experiments are planned and expected to provide new avenues for gathering insight into stress driven grain boundary migration, and the expanded use of this methodology will be the central focus of our work in the coming year.

Chemomechanics of Far-From-Equilibrium Interfaces (COFFEI)

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Funding:	$880,000

I. CHEMOMECHANICS OF LITHIUM BATTERY RELATED MATERIALS (William Woodford, Craig Carter, Yet-Ming Chiang, Meng Qu, Krystyn Van Vliet, and Sidney Yip)

Acoustic emission measurements performed during electrochemical cycling show a burst of acoustic events in monolithic sintered $LiCoO_2$ electrodes at a particular state of charge. This phenomenon is independent of the electrochemical cycling rate at low rates. These fracture events probably correlate with spontaneous micro-cracking due to the anisotropic Vegard's coefficients in $LiCoO_2$. However, acoustic events appear continuously during charging in sintered electrodes of $LiMn_{1.5}Ni_{0.5}O_4$ spinel. In the spinel material, the Vegard's coefficients are isotropic, thus the source of fracture events is currently being investigated.

Models for electrochemical shock were developed for materials that have a concentration-dependent diffusion coefficient. We have developed a statistical model of fracture in polycrystalline materials that shows good qualitative agreement with the acoustic emission results obtained for sintered $LiCoO_2$ electrodes.

II. CHEMOMECHANICS OF FUEL CELL RELATED MATERIALS (Sean Bishop, Jae-Jin Kim, Yener Kuru, Dario Marrocchelli, Pyeong-Seok Cho, Harry Tuller, Meng Qu, Krystyn Van Vliet, and Sidney Yip)

The team completed extensive thermo-gravimetry and dilatometry measurements on bulk $Pr_{0.1}Ce_{0.9}O_{2-d}$ (PCO) as function of pO_2 and temperature, and combined with earlier electrical conductivity meaurements to generate an extensive list of key thermodynamic and kinetic parameters describing defect generation and transport. On this basis, the coefficient of chemical expansion was determined. The chemical expansion properties of CeO_2 based solids were also computationally modeled using molecular dynamics and density functional theory frameworks, and the relative contributions of reduction induced cation radius size and oxygen loss were predicted. The insight gained is being used to predict how to minimize chemical expansion in fuel cell and related materials and resultant materials degradation.

The first measurements of elastic properties for oxide films under different oxygen concentrations at elevated temperatures as high as 750°C were performed. Preliminary indentation results demonstrate that the elastic modulus of PCO films decrease with decreasing oxygen concentration, consistent with oxygen deficient volume-expanded films exhibiting a lower elastic modulus.

III. STRAIN COUPLING, STRUCTURE AND CATALYTIC ACTIVITY OF OXIDE SURFACES

Controversy remains regarding the catalytic activity of SOFC metal oxide cathodes. The local electronic and crystallographic structure and surface chemistry are examined, often in-situ, by a variety of advanced analytical tools with high spatial resolution and under controlled strain to gain insight into the catalytic activity exhibited by a variety of model or well known perovskite oxides. The experimental work is being supported by density functional theory calculations.

III.1 New Insights into the Strain Coupling to Surface Chemistry, Electronic Structure, and Reactivity of $La_{0.7}Sr_{0.3}MnO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ (Jeong Woo Han, Zhuhua Cai, Yan Chen, Yener, Kuru, Sidney Yip, and Bilge Yildiz)

The chemical state, surface, and electronic structure of a model transition metal perovskite oxide system, strained $La_{0.8}Sr_{0.2}CoO_3$ (LSC) thin films, were investigated by in situ scanning tunneling spectroscopy under controlled temperature and oxygen partial pressure. Both the tensile and compressively strained LSC film surfaces transition from a semiconducting state with an energy gap of 0.8-1.5 eV at room temperature to a metallic-like state with no energy gap at 200-300 C. The transition to the metallic-like state and the relatively more enhanced DOS on the tensile strained LSC at elevated temperatures result from the formation of oxygen vacancy defects, as supported by both X-ray photoelectron spectroscopy measurements and density functional theory calculations.

The mechanistic and quantitative effects of strain on oxygen diffusion on $LaCoO_3$(LCO)(001) surfaces using density functional theory calculations were directed towards providing an improved understanding of the oxygen reduction reaction kinetics of solid oxide fuel cell cathodes. Planar tensile strain was found to reduce the migration barrier of oxygen vacancy anisotropically on the LCO(001) surface, inducing an enhanced mobility along the [1-10] direction and a suppressed mobility along the [110] direction. These insights are useful for designing strategies to control the desired anisotropic and uni-directional oxygen transport along strained hetero-interfaces.

III.2 Correlation between $SrTi_{1-x}Fe_xO_3$ surface composition, electronic structure and electrocatalytic activity (Yan Chen, Bilge Yildiz, Harry Tuller)

The goal for this study is to understand the role of surface Sr segregation on the oxygen reduction activity of the model $SrTi_{1-x}Fe_xO_3$ (STF) cathode system. Based on surface chemistry (XPS), electronic structure (STM), and impedance spectroscopy results, we deduce that the SrO-related segregated phase on the surface inhibits electron transfer to the surface oxygen adsorbates, which results in the suppression of the surface oxygen exchange rate and electrochemical activity.

III.3 In situ Investigation of Highly Active Perovskites for Oxygen Electrocatalysis in Solid Oxide Fuel Cells (SOFCs) (Ethan Crumlin, Eva Mutoro and Yang Shao-Horn)

In situ studies under SOFC working conditions are essential for obtaining a better fundamental insight into the kinetics of oxygen electrocatalysis. In situ synchrotron-based atmospheric pressure X-ray photoelectron spectroscopy (APXPS) was used to examine surface chemistry changes in LSC under controlled conditions. We demonstrated that the surface composition of these oxides can be reversibly controlled by electrochemical polarization. This finding provides insights into developing promising strategies to actively control surface related properties of complex oxides and tune the activity and selectivity of catalysts and sensors. The highly ORR active films consisting of YSZ(001)/GDC(001)/LSC(001) have been studied by in situ high resolution X-ray diffraction HRXRD upon increasing the temperature from room temperature to about 600 °C. Phase stability of the perovskite and temperature dependent strains (which significantly differ from the ones measured ex situ) have been determined.

Characterization and Modeling of Deformation Induced Damage in Titanium Alloys

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Funding: $185,000

The deformation behavior of a Ti-5Al-2.5Sn (wt.%) near-a alloy was investigated during in-situ deformation inside a scanning electron microscope (SEM). Tensile experiments were performed at room temperature 296K (23°C) and 728K (455°C, ˜0.4Tm), while tensile-creep experiments were performed at 728K (455°C) and 763K (490°C). Active deformation systems were identified using electron backscattered diffraction (EBSD) based trace analysis. Both basal and prismatic slip systems were active during the tensile experiments. Basal slip was observed for grains clustered around high Schmid factor orientations while in the tensile experiments, prismatic slip exhibited less dependence on the crystallographic orientation. The tension-creep experiments revealed less slip but more development of grain boundary ledges than in the higher strain rate tensile experiments performed at the same temperature. Some of the grain boundary ledges evolved into grain boundary cracks, and grain boundaries oriented nearly perpendicular to the tensile axis formed ledges earlier in the deformation process. Grain boundaries with high misorientations also tended to form ledges earlier than those with lower misorientations. Most of the grain boundary cracks formed in association with grains displaying hard orientations, where the c-axis was nearly perpendicular to the tensile direction. For the tension-creep experiments, pronounced basal slip was observed in the lower stress creep regime and the activity of prism slip was increased by increasing creep stress and temperature.

Deformation and Failure Mechanism of Shape Memory Alloys

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Funding: $150,000

The goal of the proposed research is to understand the fundamental mechanics driving the deformation and failure of shape memory alloys (SMAs). SMAs are difficult materials to characterize because of the complex solid-to-solid phase transformations that give rise to their unique properties, including shape memory and superelasticity. These phase transformations occur across multiple length scales and result in a large hysteresis loop, which allows these materials to store or dissipate substantial amounts of energy. In order to optimize the use of this hysteretic behavior in energy storage and damping applications, we must first have a quantitative understanding of the transformation behavior. The investigator uses new methodologies to provide the first quantitative, full-field characterizations of phase transformation across multiple length scales. Because recent investigations and theory have suggested that the hysteresis can be considerably enhanced in micron-sized samples, the proposed research pays specific attention to characterizing phase transformation at the microscale and smaller.

The investigator is using the 5-year award to conduct a comprehensive suite of experiments across multiple length scales and to tie these results to theoretical and computational modeling. We utilize new combinations of microscopy, diffraction, digital image correlation, and custom testing equipment (ultrasonic testing, miniaturized testing) to study phase transformation processes at a wide range of length scales, including very small length scales (with spatial resolution on the order of 1 nanometer). The proposed research is important from both a fundamental and a practical standpoint. SMAs are a very good example of the fact that nearly all materials are dependent on multi-scale interactions, and the lessons to be learned from these experiments are representative of a wide class of materials. Here, atomic interactions, sub-granular transformation, intra-granular interactions, localized strain banding, and macroscopic behavior are all closely linked. The quantitative information from this research will be especially useful to the numerous theoretical and computational studies of SMAs that are currently underway. In addition, the new experimental methodologies developed as part of this research are applicable to a wide range of future investigations into the mechanics of strain localization. Finally, these experiments will elucidate the change in the underlying mechanisms of phase transformation at small length scales and examine their suitability for application in microscale devices.

Localized Deformation and Intergranular Fracture of Irradiated Alloys Under Extreme Environmental Conditions

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Funding:	$303,000

The combination of radiation damage and an aggressive environment is a primary life-limiting process for structural components in nuclear reactor cores. Intergranular stress corrosion cracking in irradiated materials is one of the most important and yet poorly understood phenomena that limits the lifetime of metal alloys in these aggressive, high temperature environments. Much has been studied on the role of the environment and alloy composition, but relatively little attention has been paid to deformation mode. In fact, in many high strength alloys, deformation is heterogeneous rather than homogeneous and is a potential cause of intergranular cracking (IGC). In particular, strain localization can be a controlling phenomenon in irradiated materials under extreme conditions. The key to the IGC mechanism likely resides in the nature of the interaction between localized deformation bands and the grain boundaries. Unfortunately, this interaction is a problem that needs to be understood at the atomic scale and is very difficult to study both experimentally and computationally. In recent years, new experimental, theoretical, and computational techniques have become available to study properties at length and time scales not accessible previously. Experimental techniques are able to deal with smaller and smaller length scales, whereas simulation techniques using massively parallel processing can deal with an increasing number of atoms, and for the first time, the two approaches are merging. This convergence of simulation and experiment sets the stage for the objective of this project: to determine the basic processes by which localized deformation in irradiated materials leads to intergranular cracking in alloys in aggressive environments at high temperature.

We will (1) couple TEM characterization of dislocation interactions with grain boundaries, (2) conduct in situ deformation experiments at high temperature in the TEM, (3) perform EBSD for misorientation determination coupled with cross-correlation analysis methods to determine the strain tensor, and (4) perform atomic force microscopy to measure surface displacement with molecular statics and molecular dynamics to determine the underlying mechanisms controlling irradiation-assisted stress corrosion cracking that is assessed by experiments on irradiated samples in a high temperature, aggressive environment. Austenitic Fe-Cr-Ni-based alloys with a systematic and predetermined localized deformation structure will be used as these are well characterized and the susceptibility to cracking is controlled through the composition. As solute additions are known to have profound effects on the grain boundary deformation and cracking behavior, their effect will also be determined. Through this multiscale and multidisciplinary approach, the modes of grain boundary-dislocation interaction will be directly related to IGSCC susceptibility.

In this program, we will focus on two specific sub-objectives: (1) channel dislocation creation and termination at grain boundaries and (2) linkage between dislocation channel–grain boundary interaction and IASCC. The outcome of this program will be a fundamental understanding of the processes by which dislocation channel–grain boundary interaction leads to intergranular cracking of irradiated alloys at high temperature, which will provide a roadmap for controlling IG cracking and for developing a new class of radiation-tolerant alloys.

Nanostructure Patterning under Energetic Particle Beam Irradiation

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Energetic particle beam irradiation provides a highly controlled means of manipulating material microstructures at the nanoscale, representing an effective way to modify physical properties of materials. This research program explores the unique one step process for creating a number of different forms of patterned nanostructures by using energetic particle beam irradiation. During the previous three years, we have demonstrated particle beam induced formation of 1-D periodic surface arrays of nanodots and ripples, 2-D surface ordering nanodroplets or nanoholes, as well as 3-D networks of nanofibers and void/bubble superlattices extended underneath the irradiated surface of various types of materials. The amazing common feature in those nanopatterns is the uniformity of the size of nanoelements (nanoripples, nanodots, nanovoids or nanofibers) and the distance separating them. Our research focuses on the understanding of fundamental scientific basis for the irradiation-induced self-organization processes. Defect production and migration, sputtering, redeposition, viscous flow, diffusion and anisotropic movement of species, all of which contribute to the formation of nanopatterns, have been investigated through a combination of in situ and ex situ microscopic observations and computer modeling. In this renewed research program, we will incorporate the results of previous and ongoing research to improve the scientific understanding of the common self-organization mechanism responsible for the formation of those very different but apparently related nanopatterns under irradiation. We will also explore the potential for technological utilizations of the self-organization process by establishing relationships between the morphology of the nanopatterns and their mechanical, optical, and electronic properties. We will focus on the formation of 3-D nanopatterns under high energy electron or ion beam bombardment through new experiments, as well as continued theoretical modeling and computer simulation. We expect to gain understanding on the roles of experimental parameters (particle mass, energy, dose rate, irradiation temperature) and intrinsic material parameters in the nanoscale patterning and their dimension control. Based on this new understanding of fundamental materials science, the morphology, size, shape, density, and distribution of the ion beam induced nanostructures shall be precisely controlled. This will certainly have a great impact on the further development of innovative technological applications of nanostructures and irradiation-based material processing techniques.

Particle-Induced Modification of Complex Ceramics: Response of Materials to Extreme Conditions

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This research program on radiation effects in complex ceramics focuses on the determination of the fundamental processes by which radiation interacts with complex oxide, silicate and phosphate minerals, and ceramics. The investigations include systematic studies of radiation damage in minerals and ion beam irradiations of minerals and synthetic ceramics. The damage mechanisms and the evolution of the microstructure are investigated by a wide array of electron beam and spectroscopic techniques, mainly advanced techniques in electron microscopy, synchrotron XRD, and Raman spectroscopy. One of the new aspects of our research is the very high-energy (GeV) irradiation of materials at elevated pressures (up to 100 GPa) using diamond anvil cells. We want to establish the fundamental connection between radiation-induced and pressure-induced phase transitions, including order-disorder transformations and the formation of aperiodic domains. The model structures to be investigated include pyrochlore, apatite, and zircon, as well as their derivative and polymorphic structure-types (e.g., muratiate, reidite, and xenotime). Through an extensive network of collaborations, we routinely study other materials, such as silicon carbide and simple oxides (SnO_2), and have access to a wide variety of experimental facilities and analytical techniques.

We will especially focus on the amorphous state and characterize the different non-crystalline structure types that result from the interplay of radiation and pressure. For such experiments, we will make use of recent technological developments, such as the perforated diamond-anvil cell and in situ investigation using synchrotron sources. We are particularly interested in using extreme pressures to alter the electronic structure of a solid prior to irradiation. We expect that the effects of modified band structure will be evident in the track structure and morphology, information which is much needed to describe theoretically track-formation at a fundamental level. Finally, we will investigate the behavior of different simple-oxide, composite nanomaterials (e.g., uncoated nanoparticles vs. core/shell systems) under coupled extreme conditions. This will provide insight into surface and boundary effects on phase stability under extreme conditions. The ultimate goal is to design materials for performance under extreme conditions, such as intense radiation fields. We will use state-of-the-art in situ synchrotron diffraction techniques together with advanced transmission electron microscopy to characterize the different structural modifications, which includes crystalline-amorphous and crystalline-crystalline phase transformations. As always, a primary purpose of the research program is the education and training of graduate students, post-doctoral fellows, and research scientists.

Micro-Mechanisms and Multi-Scale Modeling of Cyclic Plastic Deformation of Magnesium Single Crystals

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Funding: $280,000

Magnesium single crystals with different orientations were studied experimentally for cyclic deformation, fatigue failure, dynamic response, and the associated microscopic mechanisms. In situ light microscopy was used along with mechanical experiments to explore the bulk twinning-detwinning process and its relationship with the macroscopic stress-strain response. Ex situ SEM, X-ray, and EBSD were used to characterize the microscopic features and evolution of twinning-detwinning evolution during cyclic loading. Original cyclic plastic deformation results and the evolution of the twinning-detwinning activity with increasing loading cycles were experimentally obtained for the magnesium single crystals with different orientations. The formation of residual twins under cyclic loading was observed and characterized. Microcracks were found to be closely associated with the formation of the boundaries of residual twins and the basal slip bands. Mechanism-based models are being developed to predict stress-strain hysteresis loops, the activities of slip systems, and mechanical twinning for cyclic plasticity and fatigue damage. The stress-strain relations were also collected under different loading rates to explore the material's dynamic mechanical behavior. In addition, polycrystalline pure magnesium and a few polycrystalline magnesium alloys were experimentally studied for cyclic deformation and fatigue under complex stress states and loading paths.

Mechanical Properties and Microstructural Evolution in Al-Li-Sc-Yb Alloys Containing Multi-Shell Nanosize Precipitates

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Funding: $154,000

Two Co-based alloys have been cast: Co-9Al-7.5W at% and Co-9Al-9W-10Ni at%. These alloys were induction melted and homogenized under vacuum at 1350 °C for 24 hours. The alloys were then furnace cooled, after which they were resolutionized at 1350 °C for 4 hours under an argon atmosphere. Both alloys were then heat treated at 650 °C. The Co ternary alloy was aged for 0 min, 10 min, 15 min, 1 hour, 4 hours, 16 hours, 64 hours, 256 hours, and 1024 hours. The quartenary Co system has been aged for 0, 1, 4, and 16 hours. Microhardness measurements have been taken on the ternary system, which showed higher hardness and, by extension, yield strength than a model Ni-Al-Cr from past work. Hardness results have also shown that precipitation kinetics in the Co-Al-W system at 650 °C are similar to that of Ni-Al-Cr at 600 °C. In addition to aging at 650 °C, the ternary Co system has been heat treated at 900 °C for 128 and 256 hours and is in the process of being aged for 1024 hours. These high temperature heat treatments are being conducted to gain insight into the stability of the γ' phase.

Preliminary work has been conducted on adapting current dynamic dislocation simulations to account for the superalloy microstructure. This includes the modeling of cuboidal rather than spherical secondary phases as well as high volume fractions (tested up to 70%) of precipitates.

First-principles density functional theory calculations have been used to pursue two paths: (1) investigating fundamental properties of the Co-Al-W γ/γ' system, including Ni, Re, and Ta additions, and (2) predicting novel alloying elements from a high-throughput approach. As anti-phase boundary energies are considered a fundamental property of γ/γ' strengthening, these values were calculated for Co_3Al and Co_3W L12. Large positive APB energies are predicted for Co_3W, and negative values are predicted for Co_3Al, indicative of unstable APB formation in Co_3Al. Calculations of the APB energy for Co_3(Al0.5W0.5) are currently underway. The thermodynamic stability of Co_3(Al0.5W0.5) L12 has been calculated in DFT with the SQS method, where it is predicted the alloy is not thermodynamically stable with respect to the stable compounds FCC Co, B2 CoAl, and D019 Co_3W. The mixing energy for adding Ni and Ta has been calculated to determine if alloying improves the stability of the L12 phase, and preliminary results show that Ni may be promising in this regard. A high-throughput study of over 70 alloying elements is currently underway, with early results suggesting Hf, Pt, and Ti may warrant further study.

Mechanisms and Modeling of High Output Shape Memory Alloys

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Funding:	$204,000

In this joint experiment/modeling effort, we are seeking to understand the fundamental microstructure-property relationships in a new class of high temperature shape memory alloys (HTSMAs) that are based on the NiTi-X alloy system. These alloys with ternary additions such as Pt, Pd, Hf have the potential for high transformation temperatures and good dimensional stability. Experimental characterization using a range of techniques, including atomic scale, high-annular dark field, scanning transmission electron microscopy (HAADF-STEM), and energy dispersive spectroscopy (EDS), has revealed a common microstructural feature of these HTSMAs—the presence of nanoscale precipitates that are coherent with the matrix. In all three systems, entirely new precipitates structures have been identified that arise due to ordering of the elements on the B2 lattice of the high temperature austenite phase. In the case of the (Ni,Pt)Ti and (Ni,Pd)Ti alloys, the precipitates we have termed “P-phase” are found to have a monoclinic unit cell with a unique, aperiodic stacking of these unit cells along <111> directions of the parent austenite. The precipitates in the Ni(Ti,Hf) alloys are still being fully characterized but are distinctly different from those in the Pt or Pd systems. Development of techniques for sample preparation and in situ TEM heating experiments have been essential for understanding the precipitate/matrix interface coherency and dislocation interactions.

In order to understand the role of the precipitates in determining the HTSMA behavior, phase field models of coherent precipitation and dislocation-precipitate interaction have been developed. Model inputs, including lattice parameters, precipitate-matrix orientation relationship, elastic constants, and free energy data, are obtained from experimental characterization, ab initio calculations, and thermodynamic databases. The shape and spatial distribution of concentration non-uniformity and stress field around the P-phase precipitates in (Ni,Pt)Ti have been determined quantitatively by the computer simulations. When the elastic interaction energy between the P-phase precipitates and a martenstic nucleus is calculated, their relative contributions to the increase in M_s (the martensite start temperature) are quantified as function of aging time and the result is compared with experimental measurements. The interactions between matrix dislocations and the P-phase precipitates are being investigated and their effect on the yield strength of the B2 matrix will be documented.

The continuum simulation effort has been two-fold. First, we aim to modify and calibrate a microstructural finite element model for high-T shape memory alloys. This involves modification of a code that has been developed and tested for the NiTi system. The primary modification is to program the crystallographic theory for a different transformation path (B2->B19). Calibration will then involve comparison of model predictions to our measurements of uniaxial stress-strain response at different temperatures. Second, we aim to study the effect of precipitates on the isothermal response and stress-biased thermal cycling response of the HTSMA systems. This is being accomplished by programming discrete precipitates into finite element simulations, based on close interaction with the phase field simulations and experimental characterization.

Combined Atomistic and Mesoscopic Study of Deformation of Body-Centered-Cubic Transition Metals: Effects of Alloying and Magnetism

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The body-centered-cubic (BCC) transition metals from groups 5B and 6B, iron, as well as their alloys, are the most important materials employed in technologies of energy production and conversion. Understanding of microscopic phenomena that govern processes of their fabrication as well as failures, acquired in materials science, physics, and chemistry, increased tremendously the efficiency of the development of new materials needed for ever progressing technologies. The goal of the present research is to advance our fundamental understanding of the deformation behavior that is, together with the fracture processes, the major failure mechanism encountered in service. The aim 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 density-functional theory is at present the state of the art when including fully the electronic structure. However, the size of the atomic blocks that can be studied and periodic boundary conditions are severe limitations when treating extended crystal defects. Hence, coarse-graining the problem such that the electronic degrees of freedom are removed and the atoms are considered to interact with each other via potentials is an essential step forward. In the present research, we employ the bond-order-potentials (BOPs). Earlier, we constructed BOPs for several non-magnetic transition metals, and the development of the BOP for iron, in which magnetism stabilizes its BCC structure, has been developed. Two entirely new developments are construction of BOPs for Fe-Cr, which is the primary structural material in advanced nuclear reactors, and construction of BOPs for B2 intermetallic compounds based on transition metals, which are all important high-temperature materials. In the latter case, we also investigate why the slip direction is different in different B2 alloy tin in spite of the same crystal structure.

In studying the plastic flow, we take as a basis that 1/2<111> screw dislocations with non-planar cores control the plastic behavior of BCC metals. Unfortunately, the core of such screw dislocations has never been observed. Hence, one of the studies is modeling a realistic thin foil employed in the high-resolution electron microscopy with the screw dislocation running through the foil. The results are then used in contrast calculations and provide the basis for interpretation of experimental observation.

In parallel, we investigate the dislocation glide at finite temperatures and strain rates. Here we consider that screw dislocations move via thermally activated formation of kink pairs. This mechanism is treated in the framework of dislocation models developed earlier but with the stress-dependent Peierls. Here the crucial step is establishment of the Peierls barrier that cannot be done uniquely just from knowledge of the Peierls stress. Hence, we employ the nudged elastic band model that we have modified significantly to evaluate the Peierls barrier within the atomistic model and link this calculation with the approach utilizing the Peierls stress calculations that are much less time consuming.

Summarizing, we first develop potentials in order to enable atomistic studies of dislocations and their glide in all non-magnetic transition metals, ferromagnetic iron, Fe-Cr, and a number of B2 intermetallic compounds. We then proceed to advance mesoscopic models of dislocation glide at finite temperatures and strain rates using the results of atomistic studies as input for construction of the stress-dependent Peierls barrier that enters these models, and we develop corresponding yield and flow criteria for crystal plasticity.

Plastic Strain Recovery in Nanocrystalline Materials

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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 that 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 scales—are not feasible.

To address this challenge, development of a new approach is proposed 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.

Turnable Hetero-Epitaxial Shape Memory Alloys

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BACKGROUND AND MOTICATION

Shape memory alloys (SMA) are an important class of active materials with emerging applications in various fields, including medicine (e.g., orthopedic bio-implants, stents, orthodontics), aerospace, and automobile. The interest in this class of material stems from two unique properties: (1) ability to recover their original shape after large deformations and (2) superelasticity or the ability to recover very high amounts of strain upon unloading. These unique properties are due to a solid-to-solid first order martensitic (diffusionless) phase transformation from a high temperature, austenite phase to a martensitic phase of lower symmetry. The martensitic phase transformation can be either thermally or mechanically induced and is characterized by a critical temperature and a critical stress and hysteretic behavior. A fundamental understanding of the atomic mechanisms that govern these processes and the ability to engineer these materials for improved performance will contribute to their widespread use in applications where mechanical actuation or damping is needed.

PROGRAM GOALS

The goal of this project is to theoretically investigate the possibility of tuning the thermo-mechanical response of shape memory materials via strain engineering through hetero-epitaxial integration of metallic alloys of different composition. In particular, we are interested in the ability to tune transformation temperature and reduced hysteresis.

MAIN RESULTS

We used large-scale molecular dynamics simulations with an accurate many-body interatomic potential to characterize hetero-epitaxial nano-laminates composed of shape memory NixAl1-x random alloys and B2 NiAl (which does not exhibit shape memory). We simulate cooling and heating of samples with various cross-sections, periodic lengths, and compositions to characterize how size and composition affect martensite and austenite transition temperatures and the associated hysteresis and transformation strain. Our results for laminates consisting of Ni63Al37 alloy with NiAl with (001) interfaces show a steep decrease in hysteresis as the volume fraction of NiAl is increased; this is accompanied by a much weaker decrease in transformation strain. A laminate with 40 at % of NiAl exhibits a reduction in hysteresis of over 80% from pure Ni63Al37 with only a ~20% reduction in actuation strain. The atomistic simulations provide insight into the fundamental reasons for such a phenomenal performance increase. These results show that hetero-epitaxy is a powerful avenue to tune the properties of shape memory materials and achieve properties not available in the bulk.

Mechanical Properties of Materials with Nanometer Scale Microstructures

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We are engaged in a 3-year program of research on the mechanical properties of materials with micrometer and nanometer scale dimensions and microstructures. This research includes an extension of our ongoing work on the mechanical properties of crystalline materials in small volumes, as well as new research on the emerging problem of mechanical properties of lithiated silicon for lithium-ion batteries. The continuing research is focusing on three outstanding questions pertaining to strength and plasticity of crystalline materials at the sub-micrometer scale: (1) the size dependence of the strength of HCP crystals oriented for easy glide, (2) the roles of pre-strain and focused ion beam damage on the mechanical properties of nearly perfect gold microcrystals, and (3) the role of grain boundaries with controlled misorientations on the nanoindentation and microcompression properties of aluminum. In the new research, we are studying the mechanical properties of lithiated silicon nanostructures using both nanoindentation and micropillar compression techniques. These studies will include ex situ studies of the mechanical properties of both crystalline and amorphous silicon, the latter with and without lithium. These experiments are being conducted under mineral oil to limit oxidation of the highly reactive lithium with the environment. We are also planning to conduct in situ transmission electron microscopy (TEM) deformation studies of these same materials using the micropillar compression technique and the PicoIndenter. To support this ongoing experimental work, we are also conducting modeling studies on the generation of residual stresses and the onset of fracture of lithiated silicon nanowires (NWs), nanotubes (NTs), and nanoparticles (NPs); these modeling studies depend critically on the fundamental mechanical properties of lithiated silicon being studied in other parts of this program.

Nanomaterial Thin-Film Structures: Fracture and Complex Environments

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Our BES-DOE program is focused on the mechanical and fracture behavior of molecular hybrid materials with the intent to exploit this understanding to design and synthesize improved hybrids with superior mechanical function. Recent progress includes the following.

HYDROGENATED AMORPHOUS SILICON CARBIDE THIN FILMS

Hydrogenated amorphous silicon carbide (a-SiC:H) thin films are attractive candidates for a number of nanoscience and energy applications, including CMOS, MEMS/NEMS, and photovoltaic technologies, due to their widely tunable materials properties and chemical inertness, but little is known about their mechanical properties. We have extensively studied the mechanical and fracture properties of a-SiC:H films with widely varying chemical compositions. We show that the elastic modulus of a-SiC:H films decreased from ~200 to ~5 GPa with increasing hydrogen concentration. While a-SiC:H films with stoichiometric composition (Si/C ~1) exhibited a decreasing fracture resistance with increasing hydrogen concentration, carbon-rich a-SiC:H films (C/Si ~ 5) exhibited a dramatically increased fracture resistance (greater than dense silica glasses) in spite of the higher hydrogen concentration (~60 at%). This increased fracture resistance was due to crack-tip plasticity in the films that is related to the presence of sp3 carbon chains as characterized by solid-state C13 NMR. Moreover, a plasticity contribution to fracture resistance can be adjusted by controlling the carbon concentration. We show that carbon-rich a-SiC:H films can also be used as a toughening layer to improve weak adhesion of a remote interface in multilayered structures. Importantly for applications in harsh environments, little acceleration in the crack growth of all a-SiC:H films was observed with increasing humidity, which is marked contrast to silica-based thin films.

NEW CLASSES OF CYCLOLINEAR POLYCARBOSILANE HYBRID FILMS

We have shown that a new class of cyclolinear polycarbosilane (CLPCS) thin films consisting of C-Si-C and C-C bonds exhibits not only superior mechanical properties but also an insensitivity to moisture-assisted cracking. Cross-linked polycarbosilane thin films were synthesized by a solution process in which spin-coated disilacyclobutane rings opened to form 3-D networks by 300°C thermal cure. CLPCS thin films exhibited an excellent thermal stability up to 400°C. CLPCS thin films showed excellent Young's modulus and cohesive fracture resistance, which are much greater than those of comparable organosilicate glassy hybrid films. More importantly, the films exhibited an insensitivity to moisture-assisted cracking, which cannot be achieved by organosilicate hybrids containing Si-O-Si bonds susceptible to moisture attack. These attractive properties make CLPCS thin film a novel and promising candidate for advanced nanoscience and energy technologies.

UV DEGRADATION OF HYBRID FILMS

Transparent hybrid organic films are ubiquitously used in solar technologies but little is known about the coupled effects of mechanical stress, moisture, and particularly, UV light on degradation mechanisms.

Using both bulk and thin films forms of poly(methyl methacrylate) (PMMA) as a model system, we characterize the cohesive and adhesive fracture energies of PMMA in complex environments, including UV irradiation. Both pre and in-situ UV exposure were found to significantly degrade fracture resistance. We demonstrate how arriving UV photons leads to increased bond rupture kinetics and increased crack propagation rates.

Radiation Response of Low Dimensional Carbon Systems

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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.

Investigating Deformation and Failure Mechanisms in Nanoscale Multilayer Metallic Composites

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Ongoing studies by our group at WSU, in collaboration with scientists at LANL, have focused on investigating a new class of NMM composites of hybrid coherent/incoherent interfaces (trimetallic systems). 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. Although these findings are promising, they are limited and further investigations are necessary. There remains a gap in our understanding of the physical origin of the aforementioned remarkable phenomena, as well as a dearth of predictive models. As there are numerous possibilities of NMM systems, the design space can be limitless if not guided by fundamental studies. In order to bridge the gap and narrow the design space, the following questions need to be addressed.

(1) How do interface structure, morphology, and imperfections determine NMM properties, and how do impurities (which may be introduced on purpose during deposition or during exposure to harsh environments) at the interface impact properties?

(2) What fundamental mechanisms control deformation and failure behavior in NMM composites, and how is that related to the type of interface and layer thickness?

(3) What physical parameters/measures can best guide the design of NMM composites (composition, interface morphology, and layering scheme) for specific applications? NMM composites may improve the service life and reliability of mechanical parts in harsh environments, which raises the following questions:

(4) How do changing environmental conditions (high temperature, H, He) impact interface properties and the overall behavior of NMM composites?

(5) How do operating conditions (pressure and strain rates) alter properties and failure of NMM composites?

In this renewal request, we intend to address these questions by capitalizing on our ongoing research on trimetallic systems and on undergoing atomistic and experimental research efforts at LANL as well as a WSU/LANL collaborative work in the area of molecular dynamics (MD) and dislocation dynamics (DD) modeling of NMM composites. We propose to expand our knowledge base and understanding of the mechanical behavior of trimetallic NMM composites with emphases on fatigue and creep-fatigue phenomena at moderate to high temperatures and with and without radiation effects.

Radiation Effects in Nanocrystalline Ceramics: Multi-Scale Model and Experiment

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The overall goal of this work is to determine the effects of radiation on the structure of nanocrystalline (nc) silicon carbide (SiC) using a multi-scale model validated against experiments. This research is motivated by previously published experiments and simulations showing that nc materials can have superior properties when compared to their coarse-grained counterparts. For example, nc-SiC has been shown to have higher hardness and/or fracture toughness when compared to bulk 3C-SiC. When it comes to radiation resistance, both enhancement and deterioration of such resistance have been reported in the literature—sometimes for nominally the same materials. In order to discover the reasons for such discrepancies in observations, it is necessary to determine how thermodynamics and kinetics of radiation-induced defects couple to the details of the microstructure.

Here, we use a multiscale modeling approach and a combination of experimental techniques to address the question of how radiation interacts with the microstructure of SiC. Thermodynamic and kinetic properties of defects in both crystalline and grain boundary regions have been investigated using state of the art ab initio methods based on the density functional theory as well as molecular dynamics (MD) simulations based on classical force fields. Atomistic simulations provided an input for rate theory (continuum) models of long-term evolution, which in turn allow comparison of modeling predictions to experimental data. In experiments, we have irradiated nc-SiC samples with Kr ions at various temperatures to determine how radiation resistance is affected by the grain size of the material. Specifically, we have investigated the resistance of SiC to radiation-induced amorphization, which was characterized using transmission electron microscopy and X-ray diffraction. The key discoveries are summarized below.

(1) Based on MD simulations of radiation cascades in a large number of nc-SiC samples with a varying grain size, we have discovered that the primary defect production from cascades is not affected by the presence of grain boundaries. This is likely because the migration barriers to defects are too high to observe segregation of defects to grain boundaries within the time scales when the primary damage settles in SiC. We concluded that the experimentally observed effect of grain size on radiation resistance will occur at relatively long time scales.

(2) Amorphization temperature in SiC is not controlled by the migration barriers of defects in SiC, as had been previously proposed. The energy landscape for defect reactions is complex, and energy barriers to defect recombination play an important role in determining resistance of SiC to radiation-induced amorphization.

(3) Grain boundaries play a dual role in radiation resistance over long (diffusive) time scales. They provide sinks for defects and, therefore, help anneal the damage and increase radiation resistance. However, grain boundary sinks lead to starvation of interstitials in the crystalline grains and to

accumulation of vacancies, which drives the system toward amorphization. Interstitial starvation has a strong signature in the response of SiC to electron radiation.

(4) During ion irradiation at room temperature, nc-SiC amorphizes at a dose comparable to that required to amorphize polycrystalline SiC, while at higher temperatures (> 370 K), nc-SiC amorphizes at a lower dose (is less radiation resistant).

(5) Grain boundary type has a negligible effect on defect production in SiC, which is in contrast to observations reported for other materials. Grain boundary type may have an effect on the long-term defect evolution. The dependence of sink strength in SiC on the grain boundary type is currently being investigated.

Using Artificial Microstructures to Understand Microstructure Property Relationship-Toughening Mechanisms in Metallic Glass

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Materials science seeks to correlate microstructure with (mechanical) properties. Various approaches have been employed to understand this correlation. A direct approach is to vary the microstructure through processing parameters and composition and characterize the effects on the mechanical properties. Often, however, the variation of processing parameters or composition affects several microstructural features, such as size, shape, volume fraction, and phase distribution, simultaneously. As a consequence, conclusions from these experiments are often limited to qualitative trends rather than quantitative theories. We propose a novel approach to study the microstructure-property relationship: use artificial microstructures which allow us to individually and independently vary parameters and thereby determine their individual effects on mechanical properties. As one example of this novel approach, we propose to study the toughening mechanism in metallic glasses. Bulk metallic glasses (BMGs) have attracted wide attention for their high specific strength and elasticity combined with good corrosion and wear resistance. But they have an Achilles' heel: an almost total lack of tensile ductility at room temperature and, associated with it, limited toughness. This is due to the absence of a strain hardening mechanism. Instead, a strain softening mechanism results in an instability by localizing shear into narrow bands, typically causing catastrophic failure along a dominant shear band. Therefore, in order to understand the shear band stabilizing mechanism, systematic and independent variation of individual microstructural features has to be carried out and the effect on the mechanical properties determined. Experimental limitations in determining the individual influences of microstructural features on the mechanical properties have prevented an understanding of the microscopic mechanism for tensile ductility in BMG heterostructures. Therefore, we propose a novel approach: creating artificial microstructures in which individual features can be varied independently and over a wide range. We are using our recently developed miniature fabrication method, which allows us to precisely fabricate 3-D samples with features ranging in size from 10 nanometers to centimeters. Test samples comprising the artificial microstructure are characterized for tension, compression, and fracture toughness in our custom-made testing equipment to quantify microstructure-property relationships.

Nanotwinned Materials for Energy Technology

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Funding:	$700,000

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 propose an integrated experimental, modeling and simulation program to examine the underlying mechanisms of plasticity in nanotwinned samples. We will employ a range of methods to create systems with differing twin morphologies and microstructures. The characterization of these systems will be carried out using a range of techniques, from microscopy to synchrotron scattering to the use of an atom probe. Mechanical testing of these samples will be 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.

The experiments will be coupled with a modeling and simulation program that includes atomistics, dislocation dynamics, and mesoscale simulations. The experiments will 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. The importance of this work, beyond the fundamental questions that will be answered, arises from the potential of these materials for use as structural materials in, for example, nuclear reactors.

Mechanical Behavior of Materials Program

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This program is focused on the development of an understanding of the mechanical behavior of next generation 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 and 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, and micro to macroscopic dimensions, and the evaluation of the suitability of these (non-biological) structures/systems for technological application.

Evolution of Grain Boundary Networks in Extreme Radiation Environments

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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 in nanocrystalline materials can substantially reduce 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 grain boundary networks consisting of a high fraction of annealing twins and twin variant boundaries can be stabilized against thermal coarsening and other grain-boundary-mediated degradation.

We are studying whether such networks of grain boundaries can also enhance microstructural stability under irradiation. This work is aimed at developing the basic science needed to address the overarching question: What must a grain boundary 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 are studying (1) the coupled evolution of grain boundary structure and point defects, using simulation, theory, and transmission electron microscopy of irradiated materials and (2) what this implies about the evolution of the grain boundary network, using spatially-resolved diffraction coupled with mesoscale theory.

The project work is using a tightly coupled combination of theory (crystallography and defect dynamics), computations (molecular dynamics and phase field), and experiment (in situ transmission electron microscopy, electron backscatter diffraction, and three-dimensional X-ray diffraction) to explore the basic physics governing the evolution of microstructures under high-dose irradiation. Using a model system (copper and its solid solution with nickel), we are exploring the interconnections among point defect and sink biases, atomic structure and strain fields associated with boundaries, energy and mobilities of different kinds of boundaries, and the role of triple junctions and quadruple nodes defining the grain boundary network connectivity. These results are being extended into a crystallographically sophisticated multiscale model of the interaction between radiation-induced point defects and grain boundaries in the context of a highly coordinated grain boundary network.

Deformation Physics of Ultrafine Scale Material

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Students:	4 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$814,000

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; (3) ductility and fracture mechanisms; and (4) thermo-mechanical stability. 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, nanoindentation, micro-tensile and micro-pillar compression testing, and electronic transport measurement; development of atomic potentials for the binary systems to be studied; and atomistic models of dislocation behavior for the unit processes involved in the deformation of the ultra-fine scale structures. This program focuses on developing understanding of the behavior of materials near their theoretical strength estimates of perfect crystals, and it should catalyze new advances in the applications of such materials. The applicability of this knowledge should impact a broad range of engineering materials, such as load-bearing structural components, advanced nuclear energy systems, and electro-mechanical systems. It seeks to inspire the development of new materials with attractive combinations of mechanical, electrical, and thermal properties.

Multi-Scale Study of the Role of Microstructure in the Deformation Behavior of Hexagonal Material, Controlled Deformation Material

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Students:	4 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$981,000

The scope of this program is to use an integrated experimental and theoretical approach to characterize dislocation and twin structures in HCP, their interactions, and the role that they play during plastic deformation. In addition to the microscopic characterization of dislocations, grain boundaries, and twins, we link the micro-macro scales by connecting these mechanisms to the overall mechanical response of polycrystals.

During FY 2011, the focus of this program has been to (a) to elucidate the basic mechanisms of twin nucleation and propagation in HCP, which are not well understood although they play a primary role in plasticity, and (b) to incorporate the micro-scale knowledge into polycrystal constitutive laws, and benchmark those utilizing complex testing histories involving changes in strain path, temperature, and strain rate.

Radiation Damage Effects in Ceramics and Non-Metal

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,026,000

The goal of this program is to understand the radiation damage response of ceramics exposed to neutrons or other energetic particles. Our studies of the damage response of ceramics address two objectives: (1) to predict microstructural evolution in ceramics exposed to radiation and (2) to identify the physical aspects of ceramics that are effective in promoting radiation resistance. Our ultimate goal is to design new radiation-resistant ceramics. We conduct neutron, ion, and electron irradiation tests on both single and polycrystalline ceramics to evaluate their irradiation damage response. We perform computer simulations of damage evolution in ceramics to assist in our understanding of radiation damage phenomena in these materials. These simulations involve a number of computational techniques. In particular, we apply accelerated molecular dynamics (AMD) to reach experimentally relevant time scales in our simulations. This allows us to assess defect mobility, annihilation, and aggregation with the goal of predicting radiation damage in non-metallic model oxides such as MgO. We have expanded these model oxide studies to examine the effects of impurities, composition, and structure on radiation damage tolerance. A new emphasis of our program involves high-temperature irradiations using energetic neutrons, ions, and electrons over a large range of radiation dose and using a variety of dose rates. We expect radiation resistant ceramics to find application in existing fission reactors, in future fusion reactors, or in ceramic nuclear fuel and waste forms.

Multiscale Mechanical Properties and High Temperature Alloy Design

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Funding:	$985,000

This project focuses on understanding the fundamental mechanisms that control mechanical behavior in metals and alloys across a variety of length scales. Of special interest are unusual phenomena that cannot be explained by conventional theories. Examples include size effects on mechanical properties, magnetic effects on strength and ductility, and stress-induced superelasticity in the absence of any obvious structural transformation. Our near-term focus is on mechanical behavior at small scales approaching those of the "unit events/processes" responsible for deformation. We utilize innovative processing techniques and state-of-the-art microanalytical tools to synthesize and characterize the structure and mechanical behavior of nano- and micro-scale materials. Theory and simulations are used to examine defect formation and behavior, and to explain their effects on mechanical behavior at small length scales. The understanding that we generate in the area of mechanical behavior is utilized to develop broadly applicable scientific principles for the alloy design of next-generation materials for use in a variety of advanced energy applications.

Radiation Tolerant Nanoclusters

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Funding:	$958,000

The objective of this program is to understand the formation mechanism, energetics, and fundamental hardening behavior associated with stable nanoclusters in metallic alloys and to establish a fundamental understanding of the mechanisms that control their response to intense irradiation. Mechanisms will be elucidated through a synergistic approach of ab initio theory, computer simulation and modeling and atomic level experimental characterization of nanostructured materials during isothermal annealing, the extrusion process, and before and after high dose neutron and ion irradiation by atom probe tomography, analytical transmission electron microscopy (TEM), and neutron scattering. This research is ultimately aimed at developing the understanding needed to enable fundamental discoveries regarding nucleation and defect mechanisms, radiation tolerance, and the interaction of helium with nanoclusters in nanostructured materials. The scientific principles developed with this research will 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 of high temperature and high dose radiation.

Crack-Tip Mechanisms Driving Environmental Degradation

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Students:	3 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$651,000

First-of-a-kind, discovery-based research is proposed 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. Recent research involving analytical transmission electron microscopy of nanometer-scale crack openings demonstrates that the existing mechanistic understanding of environmental degradation is inadequate in many circumstances. A critical change in thinking is needed to explain the nanoscopic crack-tip observations and link to micro/macroscopic behavior. It is increasingly apparent that interfacial selective oxidation in the localized and highly confined crack environment plays a significant role in the degradation process. This makes it imperative that the oxidation events at liquid-solid, gas-solid, and solid-solid interfaces be investigated to establish controlling processes. Achieving the necessary underpinning science for a seminal understanding of environmental degradation requires well-focused experimentation and simulation studies that elucidate what is occurring at surfaces and crack tips in unprecedented detail. This proposal builds on recent advances in analytical characterization, in situ and ex situ experimentation, and atomistic modeling approaches to address fundamental environment-induced degradation mechanisms.

Defects and Defect Processes in Ceramics

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Funding: $300,000

Proposed research is focused on understanding the roles of localized charge transfer and electronic excitation processes induced by incident energetic particles on charge transport, chemical and structural defect creation and evolution, and mechanical property changes in ceramic composites containing distributed and homogeneous nanophases. Results gained from ion-irradiation studies of these three-dimensional architectures underpin the design of radiation-tolerant materials not only to be used for sequestration purposes, but also for use as robust infrastructure materials in fusion and fission reactors, and for the development of stable electronic materials to be used in high radiation environments. This work is based on the premise that the collective action of charge transfer processes on the nanoscale and at multiple ceramic interfaces will indeed enhance charge transport, promote defect annihilation, and subsequently impact behavior of the material following an assault of energetic particles. Concepts will be tested by modeling the radiation response of distributed 3-D ceramic interfaces in combination with materials synthesis, ion and electron irradiation, nano-indentation, and materials characterization using innovative approaches that draw upon new and unique capabilities at the laboratory. Proposed experiments and simulations will examine effects in selected systems, provide verification of the modeling results, and subsequently enhance our understanding of key microstructural elements that resist radiation damage. Radiation effects will be studied at the nanoscale and in selected composite morphologies because it is known that these, heretofore, poorly characterized nano-materials have unique properties markedly different from those of bulk materials. This integrated approach invokes leadership-class computational methods coupled with innovative synthesis and characterization techniques to study radiation effects in materials having 3-D tailored interfaces over an extended range of energies, fluences, and temperatures.

Exploring the Radiation Damage Resistance of Nanoscale Interfaces

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Funding: $558,000

The objective of this research is to rigorously test the hypothesis that internal interfaces can be manipulated at the nanoscale to enhance recombination of radiation-produced defects to dramatically reduce radiation damage without compromising other physical and mechanical properties. This hypothesis has never been rigorously tested; in fact, there has never been a fundamental study of radiation damage at interfaces that encompasses the wide range of interface types and structures that are proposed here. In this project we seek to (1) understand defect absorption at interfaces as a function of interface character and properties; (2) determine interface ability to adsorb and delocalize point, cluster, and line defects to promote recombination; and (3) determine interface stability and evolution under irradiation. The work consists of integrated experiments and modeling of a wide range of interface types to determine how variation in interface properties such as misfit dislocation density, excess volume, and interface misorientation affect defect absorption and recombination. Tailored metal/metal, metal/ceramic, and ceramic/ceramic interfaces will be studied in order to explore the full range of interface types relevant to the materials, components, and structures found in advanced nuclear energy systems.

Mechanics of Small Length Scales

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Funding: $736,000

Nanocrystalline metals have demonstrated exceptional properties, including superior strength and fatigue resistance, compared to conventional metals. However, these nanocrystalline metals have shown a strong propensity to undergo grain growth, evolving away from the nanocrystalline state. While grain growth in conventional metals only occurs at temperatures > 40% of the melting temperature, nanocrystalline metals have been shown to exhibit grain evolution at < 5% of melting. Our core hypothesis is that the enhanced properties of nanocrystalline metals are governed in part by the stability (or instability) of the grain boundary structure.

The Nanomechanics and Nanometallurgy of Boundaries project examines the formation and evolution of defects, nanocrystalline grains, and grain boundaries in metals, and the emergence of often remarkable properties as a direct consequence of such defect and grain structure. This program integrates material synthesis, physical and structural experimental characterization, and theoretical modeling. The goal of this program is to drive towards a fundamental understanding of how grain structure at nanometer length scales develops and changes in response to driving forces, and how this structure influences the properties of the metal.

Our modeling effort provides the theoretical backbone for the project. In the past year, the modeling effort has mined our MD simulation of 388 FCC grain boundaries (bicrystals) to examine temperature-dependence of mobility and shear-coupled boundary migration. From this rich study, we have discovered a complex set of phenomena which dispel previous simple descriptions of boundary behavior. While 57% of all boundaries obey Arrhenius thermal activation of mobility, only 3% do so with a single activation energy over the temperature range of 600-1400 K. The other 43% of the boundaries behave unexpectedly showing athermal, antithermal, or thermally-damped behavior! For example, the mobility of a majority of S3 boundaries varies linearly with 1/T, suggesting thermal damping. To explore the mechanically-induced grain growth in polycrystals, the modeling effort has undertaken a herculean MD simulation of indentation-induced grain growth in nanocrystalline metals. The simulation involved 13 million atoms associated with ~1000 grains deformed over a timescale of 75 nanoseconds, representing 0.975 atom-seconds. As anticipated, the simulation clearly revealed indentation-induced grain growth at room temperature in FCC Ni.

The complimentary experimental effort has also made interesting discoveries over the past year. The high-cycle fatigue resistance of nanocyrstalline and ultrafine grained Ni-20Fe was studied as a function of grain size, ranging from 49 nm to 633 nm. This study has revealed a grain-size transition: at grain sizes larger than ~100 nm, the endurance limit varies linearly with the reciprocal square root of grain size; but for grain sizes below 100 nm, the trend reverses, leading to a peak in fatigue resistance for grain sizes ~100 nm. This emergent behavior is akin to Hall-Petch breakdown and is thought to be caused by a suppression of collective dislocation activity required for crack nucleation.

In the upcoming year, the attention of both our modeling and experimental efforts will focus on understanding the mechanisms of mechanically-induced grain boundary migration. MD efforts will examine dislocation interactions with particular grain and twin boundaries resulting in strain-induced boundary motion. The experimental effort will focus on in situ FIB and TEM observations of both thermally- and mechanically-induced boundary migration.

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:	$267,000

Exploitation of solar energy is being explored both nationally and globally, with economic solar technologies being identified by the National Academy of Engineering (NAE) as one of the 14 Grand Engineering Challenges of the 21st century. Nationally, the solar energy effort is being driven by initiatives such as the Presidential Solar America Initiative (SAI) through various programs, including the U.S. Department of Energy’s Solar Program. It is anticipated that in the future, use of organic or polymeric based photovoltaics (PVs) will provide solar technologies that are cheap enough to be widely exploited and, therefore, provide a significant fraction of future energy production needs. For organic PV (OPV) technology to meet these challenges, the efficiencies of OPV materials and devices must be enhanced several fold to make these next generation solar cells competitive with current inorganic or hybrid photovoltaics systems. However, despite considerable research efforts, the current photovoltaic efficiency of OPV devices remains limited (max reported ~ 9 %), quite apart from additional problems such as device stability.

A 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 effects. However, to achieve profound advances in OPVs, a fundamental understanding of a correlation between morphology and efficiency is essential. To address this issue, we are studying model bulk heterojunction systems consisting of mixtures of fullerenes and conjugated block copolymers (BCP). The tunability of the morphology and structure of these model systems will allow us to test fundamental issues that are currently poorly understood, and will ultimately offer vast potential for dramatic improvements in OPVs. Areas being investigated and questions and scientific issues being addressed include:

(a) How does the phase domain architecture [i.e., morphology (lamellae, cylinders, gyroid) and orientation (parallel, vertical)] correlate with OPV efficiency?

(b) BCP architecture evolves through numerous intermediate ordered states during thermal annealing that may potentially be more optimal than the final ordered structure. How do these temporally varying structures correlate to OPV efficiency?

(c) How does the efficient electron capturing fullerene impact the evolving morphology as a function of loading level?

(d) Can fullerene percolation in selective BCP domains be attained?

(e) How can simulations help us understand these issues at a fundamental level?

This proposal develops important three-way correlations that establish relationships between the complex, temporally evolving hierarchical fullerene-BCP and BHJ architecture with both the corresponding photoelectronic properties, representative of potential device efficiency, as well as the corresponding complex molecular fullerene-BCP interactions. Advanced neutron scattering and imaging techniques are being exploited to determine the detailed hierarchical structural information of model fullerene-BCP systems to address the critical questions (a-e) listed above. We perform detailed scattering studies of the temporal evolution of the BCP architecture, as well as the bulk transport controlled BCP and BHJ ordering effects. In-situ morphology studies are enabled by a high flux neutron source, such as the SNS at Oak Ridge National Laboratory. Coupling the experimental studies of the evolving morphology with extensive molecular and morphological structure modeling and its relation to photoelectronic properties will provide a substantive framework and fundamental knowledge needed to advance the design and fabrication of next-generation BCP derived OPV solar cells.

Vibrational Entropy Studies Using Inelastic Neutron Scattering

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Funding: $152,000

Vibrational thermodynamics makes an important contribution to alloy phase stability and phase transformations. It can now be studied with efficiency and accuracy. Ab-initio tools for calculating vibrations (phonons) in solids have made rapid progress, and we have been using some of them. The core of our work is measurements of phonon spectra by inelastic neutron scattering, for which impressive new capabilities are now available in the U.S., and for which we have unique expertise. Especially in combination, neutron scattering and computation allow us to identify the reasons for differences in vibrational entropies of materials. There is a set of phenomena that determine the vibrational thermodynamics of materials. Our focus is on those that are important at higher temperature and are not so well understood, especially phonon-phonon interactions and electron-phonon interactions.

Neutron and X-Ray Studies of Spin and Change Manipulation in Magnetic Nanostructures

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Funding: $320,000

This project is devoted to the use of advanced neutron and x-ray scattering and imaging techniques to study the magnetization distribution at interfaces in thin films, patterned magnetic films, nanodots, and other magnetic nanostructures. The goal is to determine the magnetic response of these systems to applied magnetic, electric fields and electric currents. Using these methods, we hope to understand the basic mechanisms governing these processes and, ultimately, how to manipulate spins in magnetic devices for more efficient information storage and processing. We are studying systems with exchange bias, tunneling magnetoresistance junctions, novel oxide interfaces, spin and charge transport at ferromagnet/semiconductor interfaces, and piezo-magnetic systems.

Novel Molecular Materials for Hydrogen Storage Applications

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Funding:	$277,000

This group has continued to investigate the high pressure behavior of Silane, Silane-Hydrogen, H_2O-Hydrogen, H_2S-Hydrogen, Xenon-Hydrogen, metal hydrides of the class $BaReH_9$, and aminoboranes using a suite of tools, including Raman spectroscopy, infrared spectroscopy, synchrotron powder, and single crystal diffraction and neutron diffraction.We conducted an extensive study of the optical, electronic, and structural properties of silane (SiH_4) to 150 GPa and concluded that, contrary to many published reports, silane is not metallic above 50 GPa but more probably decomposes in Si and H_2. If, on the other hand, careful experiments are done, it remains insulating to very high pressures with a band gap of the order of 1.0 eV at 150 GPa. Similar to the molecular compound $(CH_4)_2H_2$ first discovered by this group in the CH_4-H_2 system, we have observed the formation of $(H_2S)_2H_2$ compound with a very interesting behavior at high pressures essentially brought about by the tuning of intermolecular forces by pressure. A new clathrate structure analogous to alpha-quartz has been observed to form at pressures of the order of 1 GPa and below 120 K. This structure is closely related to the tetragonal clathrate observed in the N_2-Ar system. The compound $Xe(H_2)_{13}$ synthesized at 4.2 GPa and at room temperature was observed to be stable on complete pressure release below 90 K. This not only makes this the hydride with the highest H_2 stoichiometry but also one that is stable to temperatures above liquid N_2 temperatures (77 K), making it a technologically relevant material. We are currently investigating the structure of this using neutron single crystal diffraction. The hydrides such as $BaReH_9$, Na_2ReH_9, and Li_2ReH_9 are predicted to become metallic and show interesting properties at high pressures. The properties in this class of materials is guided by the H-H distance that is tuned with pressure and the relative incompressibility of the Re core. While optical measurements (Raman, IR, and UV-VIS transmisssion/reflectance) have shown the onset of a transition at pressures as low as 8 GPa, no further changes were found even when compressed to 100 GPa. In an effort to understand this, we are pursuing neutron diffraction of deuterated samples to elucidate the behavior of the Re-D bond and positions under pressure. While we have continued to push the efforts to understand rehydrogenation in spent BN materials using pressure, we have found, for example, mixtures of Me_2NHBH_3/H_2 hydrogenate ethylene and CO_2 above 0.5 GPa. In addition, we also explored the high pressure behavior of a number of related compounds. In particular, we used Raman, IR, and x-ray diffraction techniques to understand the orientational transitions in TMAB (tetramethyaminoborane) under pressure and could arrive at a rationalization of its unexpected high pressure stability.

Neutron Scattering Studies of Classical and Quantum Fluids in Nanoporous Media

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Funding:	$150,000

The scientific goal of this project is to reveal the role of Bose-Einstein Condensation (BEC) in creating the conditions for superflow and by analogy for superconductivity. The materials investigated are bulk liquid and solid helium and liquid helium confined to nanoscales in porous media (in disorder). Possible superflow in solid helium has recently been reported and is a current hot topic. In a unique, world class program at the Spallation Neutron Source (ORNL), at the Institut Laue Langevin (Grenoble) and less so now at the ISIS Facility (UK), we explore and establish essential benchmark data on BEC and modes for comparison with superflow measurements to reveal the interplay between BEC, modes, and superflow. Inelastic neutron scattering is, at this time, the only method of observing BEC and the dynamics of condensed helium. Two examples of progress are noted below.

(1) A Localized BEC phase in disorder: Both superfluidity and superconductivity arise from BEC, of 4He atoms in the former and of Cooper paired electrons in the latter. BEC introduces phase coherence needed for superflow. However, disorder can break this phase coherence, separating the BEC into isolated patches of BEC. This destroys the phase coherence and superflow across the sample, leaving only local phase coherence. We have shown that there is a localized BEC phase lying between the superfliud and normal phase in helium in disorder. In the LBEC phase, the BEC is localized to patches of BEC with no superflow across the sample. The LBEC phase may be analogous to the pseudo-gap region that lies between the superconducting and normal phases in cuprate superconductors.

(2) BEC in pressurized liquid and solid helium: In our measurements to date in bulk crystalline solid helium, we have not observed BEC. Observation of BEC would be an unambiguous verification of superflow in the solid. Most recently, we have measured the B-E condensate fraction, n_0, in liquid helium as a function of increasing pressure up to solidification of the liquid at 25.3 bar. In the liquid at solidification, the condensate fraction n_0 is only 3%. We have also measured the temperature dependence of $n_0(T)$ at 24 bar, showing that the momentum distribution narrows with the onset of BEC. On naive density arguments alone, n0 is expected to be very small but observable in the solid. We have created amorphous solid helium in MCM-41 porous media. As in liquid helium under pressure, both superflow and a condensate fraction are predicted to exist in amorphous helium, a possible defected solid which enables superflow. In this way, we are bringing new information on the liquid under pressure and preparing the ground for a measurement of BEC in amorphous solid helium.

Neutron Compton Scattering as a Probe of Hydrogen Bonded (and other) Systems

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Funding:	$142,000

Neutron compton scattering uses the high energy neutrons available at pulsed neutron sources to measure the momentum distribution of protons or other light ions in solids and liquids. Of particular interest are hydrogen bonded systems such as water, many ferroelectrics, and super-protonic conductors. The momentum distribution is a local probe of the environment of the proton and in some cases, allows for a complete description of this environment by providing a measurement of the 3-D potential energy surface that the proton resides on. The first such measurement has been done, and we will be exploring the systematics of the variation of this potential for the O-H-O hydrogen bond as the separation and neighboring ions are varied. This work will provide (1) the first experimental database for these potentials and (2) a means of validating or not the various theoretical methods that are used to calculate them. The information gained is essential for the understanding of a wide range of chemical and biological processes involving the making and breaking of hydrogen bonds, such as the folding and unfolding of proteins and the transcription of DNA. We have found that the interaction of water with proteins or DNA changes the quantum state of the protons as bonds are broken and made in the material and in the water. These changes are thermodynamically significant at room temperature. The quantum nature of the proton, in particular, its ability to be localized in two places at once, is manifest in many unexpected systems. These include water confined in small spaces in porous materials, nanotubes, or in the polymer electrolyte membrane Nafion, where this property may be responsible for the high conductivity of the latter material through the mechanism of “coherent transport.” The quantum state of water confined in these materials is qualitatively different from that of bulk water. We are conducting further experiments and theoretical calculations to explore this state.

Development of New Methods to Study Materials Structure using Spin Echo Scattering Angle Measurement (SESAME) of Neutrons

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Funding:	$263,000

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. For bulk samples, the method complements conventional Small Angle Neutron Scattering (SANS) and Ultra-Small Angle Neutron Scattering (USANS) because it measures a real space correlation function rather than a scattering function in reciprocal space and because it is not limited by multiple scattering corrections. For thin films, the method offers the potential for measuring Grazing Incident SANS (GISANS) to interrogate in-plane structure of thin films and buried interfaces.

Based on work we have performed over the past 3 years with DOE support, 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 0.2 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 any major neutron source. To allow spin echo angle coding to be applied to weakly scattering samples, we will develop a new method called dark-field SESAME, which will use interference between diffracted beams to eliminate most of the unscattered neutron beam from the spin echo signal.

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. These experiments will be performed using the equipment described above on neutron instruments at LENS, LANSCE, HFIR, and NIST. In addition we will carry out experiments on dedicated SESAME beam lines at the ISIS facility in the UK or at the Delft University of Technology in Holland. Systems we intend to study include mixtures of colloids and polymers that show gel, glassy, and hierarchical structures that are relevant to many industrial products such as food, cosmetics and structural materials; aggregated polyelectrolyte molecules which are similar in size to charged biological molecules that aggregate in cells, either to perform useful functions or as a result of disease; 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.

Polarized 3He in Neutron Scattering

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Funding:	$333,000

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 3He-based neutron spin filters. These devices employ lasers to polarize 3He nuclei through collisions with polarized alkali atoms and exploit the large spin dependence of the neutron-3He interaction to polarize slow neutron beams. Polarized neutron beams are very useful for neutron spectroscopy.

The number of applications of 3He neutron spin filters on neutron scattering instruments is a sensitive function of the achievable 3He polarization in a cell of reasonable neutron optical thickness. We have greatly increased the polarization and volume of polarized gas in neutron spin filters over the course of this research through a combination of advances in glass cell fabrication, laser technology, and improved understanding of the atomic physics of the alkali-3He interaction. Present neutron spin filters achieve

3He polarizations of 75-80%, not far from a theoretically-predicted maximum for the technique of around 95%. This performance is good enough to make these neutron spin filters superior to other alternatives for certain applications. The long-term support from the Office of Science for this work has led to the establishment of 3He neutron spin filters as a standard user option on a growing number of neutron scattering spectrometers at NIST and the foundation for their use on several neutron spectrometers at SNS. The scientists at the neutron scattering facilities now in charge of these devices have been drawn from the graduate students and postdocs trained through this research program.

Institute for Quantum Matter at Johns Hopkins University

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Funding:	$1,242,000

New materials have shaped human existence through the ages, from the iron age to the plastic age, from the industrial revolution and the coal age to the modern internet world and the age of silicon. As we confront challenges from unprecedented growth in global energy demand and seek to extend the essential information technology revolution, new materials built from a deep understanding of atomic scale properties will play a critical role. Indeed, while only time can tell, we may well be at the doorstep of the age of quantum materials.

The Johns Hopkins-Princeton Institute for Quantum Matter was formed in 2008 to discover and understand emergent properties in hard condensed matter with the potential for transformative impact on energy and information technologies. Over the past 3 years, we have discovered new frustrated magnetic materials and documented and analyzed their novel collective properties. IQM scientists have contributed to understanding a new class of iron-based high-temperature superconductors, defining the relevant models and determining their symmetries. In its push to advance the experimental frontier, IQM has established world class laboratories for single crystal synthesis and THz spectroscopy, and commissioned a record-breaking neutron spectrometer.

For the period 2011-2014, IQM targets two classes of new quantum materials: (1) magnetic materials where quantum correlations persist to the macroscopic scale and (2) correlated superconductivity where the electron repulsion alone culminates in vanishing of electrical resistance. While IQM is rooted in fundamental science, we select topics with the potential for breakthrough applications that transform modern society, particularly in the areas of energy and information. Quantum correlated magnets may have applications as sensors; and in quantum computing, topological insulators could be the basis for novel information storage and computing, while the high-temperature superconductors have the potential to transform the way we transport, store, and use energy.

Progress in these areas requires harmonious coordination amongst scientists with common interests but distinct capabilities and approaches. With expertise in neutron scattering from quantum materials, the project director is Collin Broholm. IQM research focuses on new materials synthesized by Robert J. Cava and Tyrel McQueen in the departments of chemistry at Princeton and Johns Hopkins, respectively. Peter Armitage probes charge dynamics with low energy photons. Theoretical expertise in broad areas of superconductivity, quantum magnetism, and materials science is provided by Zlatko Tesanovic and Oleg Tchernyshyov.

IQM tightly integrates University based research with advanced capabilities for materials characterization at National User facilities. Neutron scattering will be conducted at the Spallation Neutron Source where the IQM director is involved in coordinating hard matter research. IQM shall also utilize the nearby NIST Center for Neutron Research with special access to instruments that are ideally suited to probe IQM materials. Scientific collaborations extend domestically and throughout Europe and Asia to exchange ideas, expertise, and materials for accelerated progress.

IQM attracts the very best young scientists, as students and post-doctoral fellows. The active engagement of talented young individuals from diverse backgrounds in the development of quantum correlated materials is of commensurate importance to the direct scientific output. By coordinating and empowering key expertise in synthesis, advanced characterization, and theory, the Institute for Quantum Matter aims to discover and explain new classes of quantum correlated materials to fuel technological progress and meet pressing societal needs.

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

In 2011, we have made progress in understanding the basic physics of important quantum magnets and high-temperature superconductors.

We have grown, for the first time, single crystals of a material believed to be a two-dimensional quantum spin liquid, a solid material whose magnetic moments continue to have motion, even at absolute zero temperature. The crystal, known as herbertsmithite ($ZnCu_3(OD)_6Cl_2$), is part of a family of crystals called Zn-paratacamites. Physicists started paying more attention to quantum spin liquids in 1987, when Nobel laureate Phil Anderson theorized that quantum spin liquid theory may pertain to the phenomenon of high-temperature superconductivity, which allows materials to conduct electricity with no resistance. To test this theory, scientists have been looking for materials that preserve quantum spin dynamics down to low temperatures. We have succeeded in growing large single crystals with a new technique that we developed for hydrothermal growth in a controlled temperature gradient. The largest single crystals (up to 1 cm in length) have been used in a variety of experiments, including thermodynamic measurements and inelastic neutron scattering. With collaborators, thermal conductivity and NMR measurements have been performed. Our thermodynamic measurements on single crystals reveal a small anisotropy in the magnetic susceptibility, which allows us to deduce the primary perturbations to the spin Hamiltonian beyond nearest neighbor Heisenberg exchange. With our neutron scattering measurements of the spin excitation spectrum, we find compelling evidence that the fundamental excitations are fractionalized into "spinons" with S=1/2 instead of traditional magnons with S=1. This strongly suggests that the ground state is indeed a quantum spin liquid for this two-dimensional insulating magnet, which is a very exciting development.

In other work, we have studied superconducting cuprate single crystals with inelastic x-ray scattering. In the high-temperature superconducting cuprates, there is an intriguing interplay between different types of electronic order which may compete and/or coexist with the superconductivity. It is now believed that the unusual pseudogap region of the phase diagram is characterized by a symmetry-breaking electronic state. A rich variety of broken-symmetries have been observed in different materials, including translation, time-reversal, 4-fold rotation, and inversion. Understanding how these broken-symmetries relate to each other and which ones are universal is one of the key questions under current debate. We have recently discovered x-ray scattering evidence in the superconductor $Bi_2Sr_{2-x}La_xCuO_{6+y}$ for low energy phonons coupled to the electronic density wave order observed in prior scanning-tunneling microscopy studies. We found that the acoustic phonons with wavevectors matching the electronic density wave are anomalously broadened. Surprisingly, the scattered intensities strongly indicate that the combination of inversion and time-reversal symmetries are broken at low temperatures. The observation that more than one type of symmetry is broken prior to entering the superconducting state has profound implications for the theories explaining the physics of these systems. These measurements also reveal that the coupling to phonons provides an unexpectedly sensitive probe of the subtle electronic order in the cuprates.

Neutron and X-Ray Scattering Studies of the Liquid-Liquid Transition in Supercooled Confined Water and the Slow Dynamics in Biomolecular Assemblies

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Funding:	$296,000

During the past several years, we have extensively studied the thermodynamics and dynamics of supercooled confined water in Pressure-Temperature (P-T) phase space using elastic, quasi-elastic (QENS), and inelastic (INS) neutron scattering techniques. By confining water in nano-porous silica material MCM-41-S and around a globular protein surface as its hydration water, we can suppress the temperature of the homogeneous 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 discovered the existence of the density minimum of water (D2O) at 210K; we observed a Fragile-to-Strong dynamic crossover at TL=225K; we detected the appearance of boson peaks at and below the TL. 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 allows us to show the plausibility of a first order liquid-liquid transition line at higher pressures. We also applied QENS methods to study the slow dynamics of hydration water of three biopolymers and its relation to the so-called dynamic transition of these biopolymers. In this new project, we intend to apply similar methods to map out the entire locus of the so-called Widom line and to determine the precise location of its end point, the liquid-liquid critical point (LLCP) in the above-mentioned confined water.

We shall continue to explore the dynamics of hydration water in aged white cement pastes as a function of temperatures (especially at low temperatures), and establish the connection between its observed crossover temperature and the mechanical strength of the cement at low temperatures. It is the experience of cement industry that the functions of additives such as CDs and SPs are to confer high plasticity and flowability to cement pastes. We therefore plan to make 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.

Within the last two years, we have began to study the intra-protein phonon-like excitations and their damping in globular proteins. We continue to develop the GTEE theory for analyses of IXS spectra for protein molecules with different tertiary structures. Our objective is to establish relations between the phonon-like collective motions in these proteins and their biological functions.

Using Pluronic L64 copolymer micellar system as a model system, we shall investigate the L64/D2O micellar system for its aging behavior when we perform a sudden temperature quench from liquid to attractive glass state. We shall perform these measurements by time sliced SANS technique. We shall make use of the SANS scaled intensity plot method previously developed for the L64 micellar system to investigate the kinetic-glass transition phase boundaries in dense protein Cytochrome C solutions as a function of the protein volume fraction and at different pD values.

We have recently discovered the existence of the logarithmic decay of the self-intermediate scattering function in the ß-relaxation range (1 ps to 10 ns time range) of protein lysozyme by molecular dynamics (MD) simulation and quasi-elastic neutron scattering technique. We shall continue to use MD simulation to study the general protein dynamics in the ß-relaxation range. Our objective is to use the short time capability (1 ps to 10 ns) of NSE in SNS to measure the intermediate scattering function of different proteins directly in the time domain to confirm our previous findings and to explore the biological significance of such a logarithmic stretching phenomenon in proteins.

Thermodynamics of Self-Assembly in Globular Protein-Polymer

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Funding: $250,000

During the first few months of this project, the team has rapidly initiated research to identify optimal processing pathways for globular protein-polymer self-assembly and has partially completed a phase diagram for the model mCherry-PNIPAM materials that are the focus of this proposal. Approximately ten distinct coil fractions have been synthesized, and for three of these coil fractions, the effect of solution casting conditions was investigated in detail. The solubility of the protein, tuned by varying pH, has little effect on the self-assembly process. However, the solubility of the polymer has a large effect: casting from solutions above the PNIPAM LCST results in kinetic trapping of micellar structures regardless of coil fraction, whereas casting from room temperature solutions results in the formation of structures with a strong dependence on the coil fraction. Small-angle neutron scattering from nanostructures in solution clearly demonstrates that this temperature transition results in the aggregation and precipitation of micellar nanostructures even in dilute solution, providing insight into the origins of these kinetically trapped structures from high temperature casting solutions. Solvent annealing demonstrates the ability to transition between these structures, and these processing conditions provide the basis for the ongoing construction of a phase diagram.

Initial experiments were also performed in order to develop methods for the preservation of maximal protein structure within self-assembled nanomaterials. It was found that the addition of hydrogen bonding additives such as glycerol allows essentially 100% of the protein activity to be preserved within a solid-state material, and scattering confirms that the nanostructure remains within the material even at relatively high loading of these hydrogen-bonding "plasticizers." The order-disorder transition as a function of both concentration and temperature has also been characterized in several materials in order to understand the origin of microphase separation in these conjugate block copolymers. Below approximately 40% w/w concentration for a wide range of coil fractions, ordering is driven by the PNIPAM LCST due to micelle formation and aggregation. However, for concentrations of 40% w/w and greater, the materials are ordered at all temperatures, with an order-order transition occurring near the PNIPAM LCST for some concentrations. This complex phase behavior is being currently investigated to elucidate the fundamental protein-polymer and protein-protein interactions that underly the self-assembly process.

Crystal Growth and Scattering Studies of Model Cuprate Superconductors

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Funding:	$220,000

The PI’s group is the only one in the world to have been able to grow the sizable, high-quality crystals of the model cuprate superconductor $HgBa_2CuO_4$+d (Hg1201), arguably the most desirable high-temperature superconductor due to its high superconducting transition temperature and relatively simple crystal structure. The current work builds on the PI’s prior observation (*Nature*, 2008; preprint), using polarized neutron diffraction, of an unusual magnetic order in the pseudogap phase of Hg1201, and on the subsequent discovery of novel magnetic excitations associated with this order (*Nature*, 2010; preprint). Several present goals are to (1) obtain more detailed information about the energy, momentum, and temperature dependence of these excitations; (2) extend the hole doping range of crystals for neutron scattering work; (3) use synchrotron X-ray scattering to search for subtle charge anomalies in the pseudogap phase; (4) pursue complementary charge transport measurements; (5) provide samples to colleagues at other institutions who use complementary experimental techniques, including photoemission, Raman scattering, optical spectroscopy, and Kerr effect. At present, the PI has established more than a dozen such collaborations; and (6) pursue the crystal growth of the related double-layer compound $HgBa_2CaCu_2O_6$+d for comparative studies.

Doped Perovskite Cobaltites: A Model System for Fundamental Studies of Magnetic Phase Separation

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Complex transition metal oxides represent an exciting new frontier in condensed matter physics and materials science, as exemplified by the discoveries of high temperature superconductivity and Colossal MagnetoResistance (CMR). Due to their importance in fundamental science, in addition to their potential applications in energy technologies, these oxides constitute a major part of the DOE BES effort. During the intensive research in this area in the last decade or so it has become increasingly obvious, both from experimental and theoretical perspectives, that magnetic/electronic inhomogeneity (often referred to as magnetoelectronic phase separation (MEPS)) plays a vital role in properties such as CMR. The inhomogeneity occurs over a range of length scales, in chemically homogeneous materials, and is now considered a general feature of doped correlated systems with acute competition between multiple available ground states. In the DOE-funded effort in our group, we are seeking a complete and quantitative understanding of this magnetoelectronic phase separation, combining powerful and direct neutron scattering techniques with a wide range of complementary physical property measurements including various forms of magnetometry, electronic transport, heat capacity, etc. We synthesize materials in both bulk and thin film form, focusing on the doped cobaltites as model systems. These cobaltites span the range from the “simplest” doped perovskites (i.e., $La_{1-x}Sr_xCoO_3$), through the complex narrow bandwidth systems (e.g., $Pr_{1-x}Ca_xCoO_3$) and Ruddlesden-Popper phases (e.g., $La_{1-x}Sr_{1+x}CoO_4$), to heterostructured thin films (e.g., $SrTiO_3/La_{1-x}Sr_xCoO_3$). Our goal is a detailed, quantitative understanding of the global behavior of the magnetic inhomogeneity, employing neutron scattering techniques such as Neutron Diffraction (ND), Small-Angle Neutron Scattering (SANS), and Polarized Neutron Reflectometry (PNR).

Designer Phase Transitions in Lithium-Based Spinels

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Funding:	$141,000

During Physical year 2011, ending in May 2011 with the end of the project we accomplished the following:

Our main result was that we managed to link the response of a doped quantum critical system to the formation of magnetic clusters. In particular we showed that (1) a distribution of Kondo temperatures as present in a doped quantum critical system must necessarily lead to the formation of magnetic clusters upon approaching the quantum critical point; (2) finite size quantum effects force isolated clusters to order, rendering them impervious to Kondo shielding; (3) because of the emergence of ordered clusters that quantum critical systems will resemble percolation problems, but with the twist that only moments can be removed from the percolating cluster; and (4) this new percolation scenario leads to a new universality class from a percolation point of view, but to a sample dependent critical exponent when the approach to ordering is described.

Our findings have the potential to resolve some outstanding mysteries in doped quantum critical systems, such as why critical scaling can be observed in a sample that is above its critical dimension, why no universal exponents have been found experimentally, and why the critical exponents in stoichiometric systems appear to be those of a percolation problem. The latter statement requires further investigation, the former two are borne out by neutron scattering experiments and by numerical simulations.

Optics for Advanced Neutron Imaging

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Funding:	$325,000

We are developing novel neutron focusing optics, which can be used for neutron scattering and diffraction experiments as well as for neutron microscopy. The optics is based on grazing incidence Wolter geometries and can be used to produce coma-free neutron focusing. The mirrors are fabricated using an electroformed nickel replication technique, developed at Marshall Space Flight Center (MSFC), in which the mirror is replicated from a superpolished and figured mandrel. This neutron optics program is in collaboration with the MIT (the MIT group submits a separate abstract.)

The project at the MSFC has progressed towards three main objectives: (1) demonstrate the neutron-imaging capabilities of electroformed nickel optics, (2) develop a technique for direct replication of suitable multilayer coatings from flat and curved surfaces, and (3) develop a mandrel for the neutron mirror per the MIT group specifications.

Towards this end, Ni/Ti multilayer coatings with several different bilayer thicknesses and different numbers of bilayers per sample have been produced and characterized using an x-ray reflectivity technique. The interlayer roughness obtained was found to be between 5 and 8 A, which is an acceptable level for neutron supermirror coatings. The neutron reflectivity measurements for these coatings are planned for December 2011. The MSFC group also produced the flat and cylindrical superpolished mandrels for the replication experiments planned for the near future.

Our group is working closely with the MIT group on optimization of the optical prescription for neutron grazing incidence mirrors for small -angle neutron scattering and neutron difractometer instruments.

In order to demonstrate the imaging capabilities of the grazing incidence optics, four ellipsoid-hyperboloid pure nickel mirrors were fabricated having radii of 14.3, 15.0, 15.8 and 16.6 mm. The mirrors were nested together to form a grazing incidence microscope with a magnification of four. The imaging properties of the microscope have been tested at the instrument development beamline at HFIR (CG1-D). Magnified neutron images of the Gd grid line test sample were obtained, and analysis of these showed that the microscope was capable of resolving a period of 0.290 mm or single lines 145 micron wide.

Polarized 3He in Neutron Scattering

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Funding:	$19,000

We are extending the technique of polarized neutron scattering into new domains by continued development and application of polarized 3He 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 3He and applied these devices to a small angle neutron scattering spectrometer (SANS), polarized neutron reflectometers, a thermal energy single crystal diffractometer (SCD), and a thermal energy triple-axis instrument. Our developments have been adopted for application on the magnetism reflectometer at the SNS and for the NIST Center for Neutron Research (NCNR) 3He user capability. Results from both these programs are emerging. We have made significant progress on wide-angle polarization analysis. We have also performed several studies relevant to continuous optical pumping, including collaboration on experiments that have revealed neutron beam effects on spin filters that are continuously pumped by spin-exchange optical pumping. We contributed to an experiment on a neutron interferometer, in which the successful results obtained are directly related to both 3He cell technology and high accuracy 3He-based neutron polarimetry. Implementation of wide-angle polarization analysis is the key thrust of our current activities.

Metastable Vortex Lattices - Properties and Applications

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Funding:	$169,000

When a type-II superconductor is placed in a magnetic field, it is threaded by swirling whirlpools of electric current known as vortices. The vortices behave like massive entities, and provide a unique probe into the nature of the superconducting state in the host material. The main focus of the project is the study of the vortex lattice (VL) in two specific superconductors: MgB_2 and UPt_3. Although these materials are very different, their VLs are found to exhibit a strikingly similar behaviour. The primary experimental method used for the VL studies in this project is small-angle neutron scattering. In the following we highlight the present status of our studies of these two materials.

The VL in MgB_2 was recently discovered by our group to display an unprecedented degree of metatstability in connection with a known, second-order rotation transition. This has allowed us, for the first time, to perform structural studies of a well-ordered, non-equilibrium VL. To date we have established the ground state VL phase diagram, which disagrees significantly from theoretical predictions, requiring a re-analysis of the interplay between the two superconducting bands in this material. Furthermore the mechanism responsible for the longevity of the metastable states is being investigated, with our latest results suggesting that robust VL domain boundaries coupled with a "jamming" of counter-rotated domains as the most likely scenario. Finally we also note that measurements on MgB_2 are relatively quick and it can therefore serve as a reference material for the studies of UPt_3 discussed below.

The main goal of the studies on UPt_3 is to provide unambiguous information about the pairing in the different superconducting phases in this material. In many respects this heavy-fermion material is the paradigm of unconventional superconductivity. With three distinct phases in the mixed state the detailed order parameter in this material is not yet well-established. To date we have performed detailed measurements of the VL temperature dependence, which is currently being analyzed and compared to theoretical models for UPt_3 superconducting phases. In addition, supplementary neutron scattering studies of the electron spin susceptibility and the magnetic ordered phase are ongoing. These measurements will be continued, making use of creative field-temperature histories to prepare metastable VL configurations, as well as to induce well-defined chiral states with different chiral directions relative to the applied magnetic field.

Finally, as a supplementary activity we are exploring the use of spin-polarized small-angle neutron scattering to study the VL anisotropy in Sr_2RuO_4, demonstrating how counter to conventional wisdom, such measurements are possible due to the strong enhancement of the transverse field modulation in strongly anisotropic superconductors. These measurements will provide both the anisotropy of Sr_2RuO_4 which is still a matter of controversy, as well as a test of the exact field distribution in anisotropic superconductors.

Magnetoelectric Hybrid Modes in Multiferroics: Neutron and Ellipsometry Studies

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Funding:	$209,000

Giant magnetoelectric effects recently found in multiferroic materials present well recognized possibilities for device applications. To understand the nature of these effects and to aid design of prospective devices, studies of coupled static and dynamic magnetic and electric properties of multiferroics is of crucial importance. For this purpose, several multiferroic and magnetoelectric systems has been studied by our team in the last year.

(A) $BiFeO_3$ (BFO) is the most promising multiferroic system for room-temperature applications. While it has been the subject of intense research for many years, two of its basic properties remained unknown: the magnetic interaction parameters, and the presence of theoretically predicted local weak ferromagnetism. Neutron scattering studies of our unique large single crystals allowed us to measure both of these properties for the first time. We found that BFO indeed shows weak local ferromagnetism with a large moment of ~0.1 Bohr magneton, which is an important requirement for application of BFO in devices. We also determined the magnetic interaction constants using inelastic neutron scattering.

These results lay a strong basis for future studies of magnetism and ferroelectricity in BFO, and for applied work on novel devices based on this multiferroic material.

(B) The magnetic structure of multiferroic RMn_2O_5 (R = Y, Er) has been investigated by means of resonant soft x-ray diffraction. Energy, temperature, and azimuthal angle scans were performed in addition to reciprocal space maps on the magnetic reflection in the different magnetic phases of YMn_2O_5. We also investigated the orbital magnetic moment at the oxygen K-edge for RMn_2O_5 with both, R = Y and R= Er compositions. These moments reflect the strong hybridization between Mn 3d and oxygen 2p states. Experiments with applied electric fields are additionally presented, showing that the helical component of the magnetic structure in the CM phase of YMn_2O_5 can be reversed by the application of an electric field. However, the incommensurate magnetic reflection in the high-temperature phase is unaffected. Interestingly, this is observed only in the presence of a small electrical current, indicative of a current-induced/-enhanced switching of magnetic domains.

(C) We studied magnetic excitations in a low-temperature ferroelectric phase of the multiferroic YMn_2O_5 using inelastic neutron scattering (INS). We identify low-energy magnon modes and establish a correspondence between the magnon peaks observed by INS and electromagnon peaks observed in optical absorption [A. B. Sushkov et al., Phys. Rev. Lett. 98, 027202 (2007).]. Furthermore, we explain the microscopic mechanism, which results in the lowest-energy electromagnon peak, by comparing the inelastic neutron spectral weight with the polarization in the commensurate ferroelectric phase.

(D) Far-infrared spectra of magneto-dielectric $Dy_3Fe_5O_{12}$ garnet were studied using a combination of transmittance, reflectivity, and rotating analyzer ellipsometry. In addition to purely dielectric and magnetic modes, we observed several hybrid modes with a mixed magnetic and electric dipole activity. Using 4x4 matrix formalism for materials with Mu=/=1, we modeled the experimental optical spectra and determined the far-infrared dielectric and magnetic permeability functions. The matching condition Se*Mu(w)=-Sm*Eps(w) for the oscillator strengths Se and Sm explains the observed vanishing of certain hybrid modes at w in reflectivity.

(E) Far-infrared spectra of hexagonal $REMnO_3$ (RE=Er, Tm, Yb, Lu) single crystals have been studied in the temperature range between 1.6 K and 300 K using transmission in high magnetic field and rotating analyzer ellipsometry. The symmetry of the IR optical phonons and their oscillator strengths were determined for compounds with different RE ions. The temperature dependence of the phonon frequencies revealed a strong spin-phonon interaction in the temperature range below ~70 K. The AFM and crystal field optical transition frequencies, their oscillator strengths, and effective g-factors have been measured using external magnetic fields up to 10 T. The frequency of the AFM resonances increases systematically with a decrease of the RE ion radius. The observed effects are analyzed taking into account main magnetic interactions in the system including exchange of the Mn^{3+} spins with RE^{3+} paramagnetic moments. The magnetic ordering of RE ions (RE=Er, Tm, Yb) was observed at very low temperatures T<3.5 K and in strong external magnetic fields.

Using Neutrons as a Probe to Study Magnetic Excitations in Strongly Correlated Electron Materials

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Funding: $220,000

Understanding the electronic structure and magnetism in doped transition metal oxides and other correlated electron materials continues to be at the forefront of modern condensed matter physics. Compounds containing quasi-localized d-electrons exhibit wide range phenomena such as high-transition temperature superconductivity and multiferroic effects. Understanding the microscopic spin excitations in these systems is central to understanding their exotic macroscopic properties which continue to defy conventional Fermi-liquid description. Neutron scattering plays an important role in determining the dynamical spin properties in these materials. The normal operation of the new spallation neutron source and upgraded high-flux isotope reactor at Oak Ridge National Laboratory have created a unique opportunity for the University of Tennessee to establish a strong materials synthesis and neutron scattering program. We propose to study spin excitations in Fe based superconductors with the ultimate purpose of understanding magnetic interactions in these materials and the training of the next generation of neutron scattering scientists. We also propose to establish a materials growth laboratory capable of producing some of the best Fe-based superconductors for the US condensed matter physics community.

Neutron Scattering Study of Unconventional Superconductors

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Funding: $200,000

This proposal is to study unconventional superconducting and their isostructural materials using neutron scattering. The newly discovered Fe-based pnictide superconductors show a number of similarities to and differences from the most well-known unconventional superconducting cuprates. In both systems, the relation between magnetism and superconductivity seems to hold the key to understanding the microscopic mechanisms for the superconductivity. We will focus on three systems: an ambipolar cuprate Y1- zLaz(Ba1-xLax)$_2$Cu$_3$Oy (YLBLCO), a superconducting Fe pnictide FeTe1-xSex, and nonsuperconducting (La,Ce)MnAsO. The ambipolar YLBLCO provides a unique opportunity to study essential differences in electron- (n-type) and hole-doped (p-type) cuprates by allowing us to easily move from n-type to p-type by controlling the oxygen content. We will study how the magnetic ground state evolves as the nature of the charge carrier changes. Large single crystals of the new Fe-based superconductors are now beginning to be available in the chemical form of Fe1.01Te1-xSex, which allows us to investigate in detail the relation between magnetism and superconductivity using intensity-limited inelastic neutron scattering techniques. We will study how the magnetic correlations and lattice vibrations change upon doping Se by performing elastic and inelastic neutron scattering experiments on the system with several Se concentrations representing the spin-density-wave and the spin-glass and the superconducting phases. (La,Ce)MnAsO that is non- superconducting but isostructural to the superconducting (La,Ce)FeAsO system will also be studied for this project.

Spin Transitions, Phase Competition and Ordering in Perovskite Oxides

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Funding: $220,000

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. Several systems have been investigated during this calendar year, ranging from complex oxides to the new class of Fe superconductors and related compounds. To explore the correlation of nanoscale atomic inhomogeneities to properties, we applied experimental tools that provide structural information at different length scales, as well as time scales. High intensity pulsed neutron as well as reactor-based neutron facilities have been instrumental in visualizing static structures and dynamics. The integration of such facilities in our research program has been instrumental to understanding the origin and mechanism of the microscopic interactions and their relation to the macroscopic properties in a select group of material. This included two classes of the Fe-based superconductors, the pnictides and chalcogenides, the perovskites that exhibit insulator-to-metal transition (IMT) transitions such as the cobaltites, the layered cobaltates (214 structures) that exhibit charge and spin ordering, the Cu and Sn anti-perovskites that exhibit negative thermal expansion, and the multiferroic $LuMnO_3$.

The program has been guided by specific questions addressing issues relating to the formation of intrinsic structures as the following: what is the nature of electron-phonon coupling and what kind of information can be extracted from local distortions? What is the relation of the structure with the observed phase transitions? What mechanism(s) mediate spin-lattice coupling, possibly leading to symmetry breaking? How strong should the distortions be to cause inhomogeneous patterns? Sometimes, distortions resulting from Coulomb repulsions can be quite subtle but their cooperative long-range effects can induce substantial strain. Other times, the distortions can be quite strong as in the Jahn-Teller type, with either cooperative long-range ordering or with local but randomized displacements. Our experimental tools allow us to make significant contributions in this regard.

Self-Assembly of Conjugated Polymer Networks:A Neutron Scattering Study

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Funding: $173,000

Solar energy, in the form of photovoltaics, is well suited to take on a central role in resolving our future energy problems. Nevertheless, significant efforts are still required to develop solar energy technologies that can accelerate the growth and competitiveness of photovoltaics in the renewable energy sector. This project involves a fundamental morphological investigation of self-assembling pi-conjugated polymers that can be utilized for the creation of efficient polymer-based solar cells. These types of solar cells could significantly reduce the cost of manufacture through the use of established coating processes facilitating the production of large area devices.

One of the primary factors affecting solar cell performance is the structure of the active layer. This structure is determined largely by the self-assembly of conjugated polymers in solution. Therefore, the performance of polymer solar cells is intimately linked to polymer self-assembly. The main purpose of this research is to obtain a fundamental understanding of poly-3-alkyl-thiophene (P3AT) self-assembly and structure development occurring over multiple length scales and environmental conditions. In particular, we focus on the fibrilar gel phases that are created when conjugated polymers are dissolved at high concentrations (> 1wt%) in solvents of intermediate quality. A central hypothesis driving this research is that the large interfacial area and the inherent interconnectivity that is provided by the gel networks are ideal structural features for device performance. Despite their optimized structure, the rheological properties of these elastic network materials can make it challenging to coat and produce thin films for use in devices. Therefore, we are also developing new routes to generate networks of conjugated polymers inside the confined environment of oil-in-water emulsions. This strategy is aimed at overcoming the intrinsic difficulties of coating gelled materials while still providing structural control over the network structures. In this program we aim to correlate multi-scale structural features of conjugated polymer networks formed in bulk and in confined environments with their rheological, optical and electronic properties. In-situ and ex-situ scattering of neutrons (SANS and USANS) and x-rays (SAXS and WAXS) are used to seamlessly probe structural features in these materials at the molecular, fiber and network levels spanning a wide range of length scales (0.1-10,000 nanometers) and sample compositions. Ultimately, we aim to provide an unequivocal link between the macro-properties and the mesostructure of organogel networks formed from conjugated polymers.

DOE National Laboratories

Correlations and Competition Between the Lattice, Electrons, and Magnetism

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Students:	3 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$1,330,000

The properties of modern novel materials, such as high-temperature superconductivity, multiferroicity, and colossal magnetoresistivity, 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. Within this

FWP, neutron and x-ray scattering are used to directly investigate the structural, electronic, and magnetic aspects of complex ground states, excitations, and phase transitions. The varied expertise of the PIs is employed in a synergistic approach, and systems are studied using a wide range of complementary 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. Topics investigated include unconventional superconductivity in iron-arsenide compounds, metal-insulator transitions and multiferroicity in correlated electron oxides, and complex magnetism in rare-earth intermetallic compounds. The program supports the HB1A spectrometer at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory and the MUCAT sector at the Advanced Photon Source (APS) at Agronne National Laboratory.

Neutron and X-Ray Scattering

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Funding:	$2,628,000

The Neutron and X-ray Scattering Group uses neutrons and x-rays to investigate the structure and dynamics of bulk and interfacial materials with properties that impact energy use, such as superconductivity, magnetism, thermoelectricity, and bio-transport. The goal is to harness the complementarity of neutrons and x-rays to study complex phenomena with a particular focus on the role of phase competition in generating functional properties. 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, artificial heterostructures, or phase-segregated biomembranes. 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. The research programs concern (a) Phase Competition in Bulk Materials (R. Osborn, S. Rosenkranz, E. A. Goremychkin, O. Chmaissem), (b) Phase Competition in Interfacial Materials (S. te Velthuis, U. Perez-Salas), and (c) Materials for Energy Applications (R. Osborn, S. Rosenkranz, E. A. Goremychkin, U. Perez-Salas, B. Dabrowski, O. Chmaissem).

Neutron Scattering

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Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $2,150,000

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.

In the past year, neutron scattering experiments have been performed at the Spallation Neutron Source and the High Flux Isotope Reactor at Oak Ridge, as well as at the NIST Center for Neutron Research. They have largely addressed the nature of magnetic correlations in superconducting crystals, as well as the more general (and related) problem of understanding itinerant magnetism. A number of studies have been done on the superconducting family $Fe_{1+y}Te_{1-x}Se_x$, exploring the magnetic correlations from the parent antiferromagnet $Fe_{1+y}Te$ through the superconducting regime, with Se concentrations up to $x = 0.65$, using single crystals grown at Brookhaven. Work is continuing on samples with partial substitution of Ni or Cu for Fe. Crystals of the recently discovered superconductor $KxFe_{2-y}Se_2$ have been grown and preliminary measurements have been done.

Turning to superconducting cuprates, neutron scattering experiments have investigated details of the spin correlations in $La_{2-x}Ba_xCuO_4$ with $x = 0.095$ and in $La_{2-x}Sr_xCuO_4$ with $x = 0.04$. Complementary high-energy x-ray diffraction measurements have been performed at HASYLAB on magnetic-field-induced charge-stripe order in closely related samples. In a slightly different direction, the first large single crystal of the multiferroic material $BiFeO_3$ has been grown, and preliminary characterizations have been performed.

Complex Electronic Materials

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Funding:	$1,750,000

Competing interactions that non-linearly couple spin, charge, orbital, and lattice degrees-of-freedom create complex and collective states that pose significant scientific challenges and underpin national energy and defense missions. Changes in material composition, dimensionality, temperature, pressure, or magnetic field tune the balance among competing interactions and induce transitions between broken-symmetry and complementary uniform states. Such complex behaviors are most pronounced near magnetic/non-magnetic and metal/insulator boundaries in electronically correlated materials and become particularly poorly understood as these boundaries are tuned to absolute zero temperature (i.e., to a quantum-critical point). Research focuses on developing a fundamental understanding of collective quantum states of complex electronic materials, especially strongly correlated f-electron systems, by exploring new materials that reveal essential new physics and by applying a necessarily broad range of experimental techniques, often at simultaneously very low temperatures, high pressures, and high magnetic fields. Complementary spin (neutron scattering and NMR) and charge (ARPES) spectroscopies probe the complex states at a microscopic level. Though studying correlated 4f- and 5f-electron systems as prototypes of complex electronic materials, this project also pursues related issues in correlated d-electron materials, with complex transuranic compounds bridging the physics of more localized 4f and more delocalized d-electron systems. DOE national facilities as well as special facilities at Los Alamos benefit this research, which is leveraged through an extensive network of experimental and theoretical collaborators.

Physical Behavior of Materials

Institutions Receiving Grants

A Surface Stress Paradigm for Studying Catalyst and Storage Materials Relevant to the Hydrogen Economy

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Funding:	$100,000

This program is focused on the understanding and development of materials relevant to the future hydrogen economy with a perspective based on a proposed surface paradigm. A large portion of the physical and chemical processes required for the hydrogen economy occurs at surfaces: steam reforming of fossil fuels on Ni catalysts, hydrogen dissociation at Pt based catalysts in PEM fuel cells, and hydrogen storage via adsorption and uptake in metal hydrides. The physisorption or chemisorption of species and the concomitant interaction always leads to a modification of the thermodynamic surface stress. This fact can be exploited as a powerful spectroscopic method for studying existing and potential catalysts and hydrogen storage materials. In-situ, real-time stress measurements have recently been used to directly measure the elastic component of adatom-surface interaction during homoepitaxial growth of several transition-metals in an ultra-high vacuum environment. In this project we will demonstrate how real-time high-sensitivity surface stress measurements can give a direct measure of a range of phenomena. More specifically, research will examine the adsorbate-surface interaction, interaction between like and unlike adsorbates, reaction thermodynamics such as activation barriers and reaction driving forces for dissociation and oxidation reactions, reaction kinetics, and relative exposure in bi-functional catalysts; all obtained through surface stress measurements and supporting electronic structure calculations. We will combine our developed understanding of surface stress effects with our understanding of transition-metal electronic structure to examine the connection between surface stress and catalytic activity, and based on our findings suggest more effective catalysts. The project will examine the fundamental connection between stress and structure evolution associated with catalyst cycling and degradation. In addition, research will examine the elastic response associated with the intercalation of hydrogen into hydrogen storage materials. By understanding the physical phenomena that lead to the kinetics and degradation of storage materials a direction for improvement of these systems should emerge.

High Performance Bulk Thermoelectric Materials

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Funding:	$150,000

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 study two materials: $YbAl_3$ and CoSi, that have thermoelectric power factors of 180 µW/(cm K^2) (YbAl3) and 80 µW/(cm K^2) (CoSi). Such high power factors are at least twice the best commercially available $Bi2Te_3$-based materials, which will 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. Besides these two materials, we are also studying other interesting materials, such as p-type half-Heusler. We also propose to study solar radiation absorbing materials to be used together with the thermoelectric materials.

Metamaterials as a Platform for the Development of Novel Materials for Energy Applications

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Funding:	$100,000

The PI proposes to explore the fundamental properties of metamaterials and their potential for energy applications. 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, materials science, to nanoscience. The PI proposes to exploit these new possibilities to engage in basic research of the experimental and theoretical properties of metamaterials and to provide a knowledge base for the discovery and design of new materials with novel structures, functions, and properties. The proposed research activities emphasize the computational design and fabrication of the materials, and the characterization of their electromagnetic properties.

Hybrid Inorganic Nitride Organic Semiconductor Heterostructures

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Funding:	$210,000

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 proposal 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 IIInitride 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 applications, both established such as solid state lighting, but also 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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Funding: $150,000

Since 2001, there has been an explosive growth of scientific interest in the role of surface plasmons in optical phenomena including guided-wave propagation and imaging at the subwavelength scale, nonlinear spectroscopy and ‘negative index’ metamaterials. The unusual dispersion properties of metals enable excitation of propagating surface plasmon modes both near and away from the plasmon resonance. At frequencies near the plasmon resonance frequency, the excited localized resonant modes in nanostructures access a very large range of wavevectors over the visible and near infrared frequency range. Both resonant and nonresonant plasmon excitation allow for light localization in ultrasmall volumes in metallodielectric structures.

To date, little systematic thought has been given to the question of how plasmon excitation and light localization might be exploited to advantage in photovoltaics. This proposed effort aims to change that. Using insights derived from the rapid developing plasmonics field, we seek to dramatically modify the light absorption and carrier collection characteristics of photovoltaic materials and devices. In particular, the ability of plasmonic structures to localize light at subwavelength dimensions is synergistic with use of ultrathin quantum dot and quantum well photovoltaic absorber materials.

Conventionally, photovoltaic absorbers must be optically ‘thick’ to enable nearly complete light absorption and photocarrier current collection. They are usually semiconductors whose thickness is typically several times the optical absorption length. For silicon, this thickness is greater than 100 microns, and it is several microns for direct bandgap compound semiconductors, and high efficiency cells must have minority carrier diffusion lengths several times the material thickness. Thus solar cell design and material synthesis considerations are strongly dictated by this simple optical thickness requirement. Dramatically reducing the absorber layer thickness could significantly expand the range and quality of absorber materials that are suitable for photovoltaic devices by, e.g., enabling efficient photocarrier collection across short distances in low dimensional structures such as quantum dots or quantum wells, and also in polycrystalline thin semiconductor films with very low minority carrier diffusion lengths.

Another interesting feature of plasmonic structures is that 1) they are metallic and thus can be used as a conducting contact to a photovoltaic absorber layer and 2) by appropriate design of shape and dielectric environment, the plasmon resonance can be broadly tuned across the visible and infrared frequency range. Thus one could design metallic contacts whose plasmon resonant spectral absorption features are well-matched to the photovoltaic absorber properties, e.g., rendering metallic contacts more transparent at photon frequencies at or above bandgap for strong absorbers by designing the plasmon resonance frequency to lie below the bandgap frequency.

Conversely, by tuning the plasmon resonant frequency of a metallic nanostructure to coincide with the bandgap frequency of a closely-coupled semiconductor quantum dot or quantum well absorber the spectral absorption of weak absorbers can be resonantly enhanced.

Functional Domain Walls as Active Elements for Energy Technology

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Funding:	$150,000

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.

My award started in July 15, 2011. Since then, we have made the following progress:

(1) We study field-effect transistors realized from VO_2 nanobeams with HfO_2 as the gate dielectric. The work was published: S. Sengupta, K. X. Wang, K. Liu, J. Wu, and M. Deshmukh, Field-effect modulation of conductance in VO_2 transistors with HfO_2 as gate dielectric; *Applied Physics Letters*, 99, 062114 (2011).

When heated up from low to high temperatures, VO_2 undergoes an insulator-to-metal transition. We observe a change in conductance (6%) of our devices induced by gate voltage when the system is in the insulating phase. The response is reversible and hysteretic, and the area of hysteresis loop becomes larger as the rate of gate sweep is slowed down. A phase lag exists between the response of the conductance and the gate voltage. This indicates the existence of a memory of the system and we discuss its possible origins.

(2) We quantified, for the first time, heat loss rate between a nanoscale solid and gas. The work was published: Chun Cheng, Wen Fan, Jinbo Cao, Sang-Gil Ryu, Jie Ji, Costas P. Grigoropoulos, and Junqiao Wu, Heat Transfer across the Interface between Nanoscale Solids and Gas, ACS Nano, in press (2011).

When solid materials and devices scale down in size, heat transfer from the active region to the gas environment becomes increasingly significant. We show that the heat transfer coefficient across the solid – gas interface behaves very differently when the size of the solid is reduced to the nanoscale, such as that of a single nanowire. Unlike for macroscopic solids, the coefficient is strongly pressure dependent above ~ 10 torr, and at lower pressures it is much higher than predictions of the kinetic gas theory. We quantified the heat loss rate across the nanowire-air interface, and found that it dominates over all other heat dissipation channels for small-diameter nanowires near ambient pressure. As the heat transfer across the solid – gas interface is nearly independent of the chemical identity of the solid, the results reveal a general scaling relationship for gaseous heat dissipation from nanostructures of all solid materials, which is applicable to nanoscale electronic and thermal devices exposed to gaseous environments.

Investigation of p-type Sb-doped ZnO Thin Films for Solid State Lighting

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Funding:	$120,000

Semiconductor light emitting diodes (LEDs) are an energy-saving alternative to incandescent and fluorescent light. Besides the traditional gallium nitride for solid state lighting, zinc oxide (ZnO) materials are receiving significant attention due to their unique properties such as wide band gap and large exciton binding energy. This renewal proposal requests support to continue successful work toward reliable p-type ZnO-based materials. In the next phase of research, we will focus on gaining complete knowledge on p-type Sb-, Ag-, and N-doped ZnO and MgZnO thin films by plasma-assisted molecular beam epitaxy. We aim at (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 toward the development of commercially viable LEDs based on ZnO and MgZnO materials for solid state lighting.

Study of Materials and Interface Properties for High-Efficiency Spin Injection

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Funding:	$130,000

In FY2011, the PI's research has focused on the study of two types of materials related to spinotronics: carbon base materials mainly single- and multi-layer graphene, and pure and doped topological insulators.

In the former, our objective is to demonstrate coherent spin transport in molecular materials and tune the charge and spin transport in carbon based materials. Different approaches have been taken to enhance the mobility of graphene, which include using high dielectric constant (e.g., $SrTiO_3$) substrates and using ligand-bound magnetic nanoparticles. In hybrid spin valve devices ($La1-xSrxMnO_3$ or LSMO-multilayer graphene- cobalt), we demonstrated ~ 12% magnetoresistance at low temperatures (25 K). In ligand bound Fe_3O_4 nanoparticle systems, we demonstrated 21% room temperature magnetoresistance and molecular length independent spin transport. The graphene work has resulted in two published papers (one in Nano Letters and the other in PRB). Two papers are currently under review (one in *Physical Review Letters* and the other in *Physcial Review B*). The nanoparticle work has appeared in Appl. Phys. Lett.

In topological insulators, we aim to use the strong spin-orbit coupling to control the spin degree of freedom in hybrid devices. But as the first step, we have grown high-quality single crystals of $Bi2Se_3$ and

Ca-doped Bi2Se$_3$. We have demonstrated a wide range of tunability in carrier density and the position of the Fermi energy. Then we have fabricated nanoscale devices and tuned the carrier density by electrostatic gating. By controlling the carrier density, we have successfully shown a sharp mobility contrast between the ordinary bulk carriers and the surface carriers, which is the transport evidence of the suppressed backscattering of predicted massless Dirac fermions in topological insulators. This work has resulted in two papers (on in *Applied Phjysics Letters* and the other in *Frontiers of Physics*). One submitted paper is currently being reviewed by Phys. Rev. Lett.

The DOE supported research has resulted in four APS March meeting talks by graduate students, and several invited talks. One at Peking University's international workshop on "The World of Hall Physics" in June and the other in Tsinghua University's workshop on "Topological Insulators and Topological Superconductors" in August.

Dipolar Ferromagnets for Magnetocaloric Effect Nanocomposites

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This research program had two thrusts, with investigations of the magnetostatic coupling of nanoparticle assemblies, and of the magnetocaloric effect in phase transitions of composite materials.

Dipolar ferromagnetism was studied in self-assembled arrays of 13 nm magnetite nanoparticles separated by 1.5 nm surfactant barriers, micron-sized magnetic domains using electron holography and Lorentz electron microscopy. Domains were visible up to a dipolar ferromagnet-to-superparamagnet transition temperature of 575 °C, and the magnetic order parameter showed a phase transition similar to that of an exchange-based ferromagnet. While a nanoparticle-based composite with uniform dispersion and strong magnetostatic coupling will have a magnetically ordered state and a collective phase transition, the change in magnetic entropy in the phase transition is too small to be competitive for applications of the magnetocaloric effect. In a dipolar ferromagnet phase transition, the monodomain particle moments disorder, but the entropy is much less than that at a Curie temperature, where all the atomic spins disorder.

Candidate materials for magnetocaloric effect applications have a Curie temperature near room temperature, and here two materials meeting this requirement were studied, MnP and NiMnGa alloys. Nanoparticles of MnP were synthesized, but they were found to be superparamagnetic at room temperature, and therefore larger grained materials were the focus of the investigation. Energy-saving applications applying the magnetocaloric effect (MCE) would be limited to the magnetic entropy change in the field of a permanent magnet (maximum 2 tesla). Many of the prototype MCE materials, Gd_5Si2Ge_2, MnFe(P,Ge), and Ni-Mn-Ga systems, though not for La(Fe,Si)$_{13}$, have anisotropic saturation fields. Our work on the MnP system showed how the crystallographic orientation of the grains affects their ability to saturate at low fields, and therefore the amount of magnetic entropy that can be used for cooling. Here the saturation field was less than 2 tesla along only one of the crystal axes, and with random orientation within a composite, the cooling performance would be degraded relative to that of a single crystal. The existence of preferential crystallographic alignment in hot pressed and die upset

MnP was investigated using magnetic measurements and electron backscatter diffraction. Pole figures showed that die upsetting causes the <110> directions to align preferentially along the die upset (DU) direction with the <001> direction preferentially perpendicular to the DU direction. Since the low-field magnetocaloric effect in single crystals of MnP has been shown to be greatest along the <010> direction and smallest along the <100> direction, this technique offers a means to achieve the advantages of single crystal alignment with the economy of using bulk processing techniques on polycrystalline material.

Because of the nature of the coupled, first-order magnetic and structural phase transitions in MCE materials, the transforming grains induce a strain on their neighbors resulting in a distribution of critical temperatures throughout the sample. This broadening is not desirable because the cooling power of MCE materials is directly related to the sharpness of the phase transition. Additionally, these strain effects lead to greater hysteretic losses and contribute to the crumbling of the material over multiple cycles. $Ni_{55}Mn_{20}Ga_{25}$ has a first-order ferromagnetic to paramagnetic and coupled tetragonal to cubic Martensitic phase transition at 335 K. High-energy diffraction microscopy microstructure mapping combined with absorption tomography was used to investigate the evolution of the microstructure at five temperatures throughout its structural and magnetic phase transitions. The results showed the phases of the grains (tetragonal versus cubic), their relative orientation, and the local strain. Even with a single cycle through the transition temperature, the material showed high local misorientation indicating a shear within the grains. The effect of repeated thermal cycling on the magnetocaloric effect in Ni54.3Mn20.1Ga25.6 was investigated. Over the course of 37 thermal cycles through the martensitic transition the moment of the sample decreased monotonically. We attribute this feature to small volumes of the sample remaining in the non-magnetic austenite phase after repeated cycling. Although the magnitude increased, the widths of the entropy peaks were slightly decreased resulting in the same refrigeration capacity as before cycling. The relief of strain through multiple cycles requires the grains to crack away from their neighbors. The crumbling during multiple cycles through the martensitic phase transition does not have a detrimental effect on the magnitude of the MCE or the refrigeration capacity.

Crystallization and Thermoelectric Transport in Silicon Microstructures and Nanostructures Under Extreme Electrical Stress

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Funding:	$128,000

This project consists of a combination of experimental and computational studies toward (1) evaluating the possibility of growth of single-crystal silicon micro-structures through melting by self-heating with short duration voltage pulses, and (2) understanding thermoelectric phenomena in micro/nano-structures under extreme conditions.

Our preliminary studies on growth-from-melt of micro-structures with micro-second voltage pulses showed strong asymmetry in melting along the length of symmetric micro-bridges for certain voltage levels. We have verified the asymmetry in the thermal profile through observation of light emission from the structures when a low-frequency high-amplitude AC signal was applied across the wires. The micro-wire/micro-bridge structures always show significantly more heating at the terminal where the charge carriers enter in both experiments, consistent for n-type and p-type structures. These two independent observations of extreme asymmetry support the premise that this asymmetry is due to strong thermoelectric effects.

During the first year of the project (~FY 2011) we have developed a high-temperature setup for simultaneous measurement of Seebeck coefficient and resistivity of thin films and a Hall measurement setup. We have also correlated experimental current-voltage measurements on micro-structures with simulations to extract thermal and electrical conductivities at elevated temperatures. We have used these extracted temperature dependent parameters in the modeling of the self-heating process.

The physical models include drift-diffusion and linear thermoelectric contributions using experimental and calculated materials properties including the abrupt changes due to the solid-liquid phase transition and the accompanying latent heat of fusion. The effects of velocity saturation and phonon-drag are also evaluated. Our modeling suggests that the contributions due to bipolar conduction at elevated temperatures and strong carrier generation upon melting –and the resulting diffusion currents, drastic changes in Seebeck coefficient and resistivity- play a critical role in the generation of the asymmetric thermal profiles. Our experiments indicate that this asymmetry is stronger at small current levels that are sufficient to melt these structures in microseconds.

One journal article with some of these results is published in the *Journal of Materials Research* as an Invited Feature Paper and three other manuscripts are currently under preparation. The findings from this project are expected to contribute to the development of fabrication techniques for higher-efficiency lower-cost solar cells and low-power consumer electronics as well as fundamental understanding of thermoelectric phenomena which is relevant to direct heat-electricity conversion and solid-state cooling.

Complex Amorphous Transition-Metal Dielectrics

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Funding:	$190,000

Our study of mixed-cation amorphous dielectrics has led to the discovery that the dielectric constant of amorphous Ta_2O_5 increases from k=23 to a value as high as k=30 when as little as ~5% Ge is incorporated in the sputtered thin film. This is unprecedented in amorphous materials, and is surprising because GeO_2 has a much smaller dielectric constant than Ta_2O_5. In order to understand the microscopic origin of this effect we have precisely determined the atomic volume, the electronic polarizability, and the ionic polarizability of amorphous Ta1-xGexOy over the range 0.3 < x < 0.97 using a codeposited composition spread. The results indicate that the dominant effect is a rapid increase in the ionic polarizability for small Ge substitutions. We interpret this as reflecting changes in local atomic bonding structure. Such changes in local structure are consistent with the small changes seen in the electronic polarizability and atomic density and are consistent with the much larger effect on the inferred ionic polarizability, as introduction of tetrahedral GeO_4 bonding could introduce new soft vibration modes. We are currently extending this study to other substitutions (e.g., Ta-Si-O and Hf-Ge-O) to see if consistent trends obtain. We have procured a Ta.95Ge.05 metal target to reproduce the results using single-target reactive sputtering. The target will allow us to prepare films with a uniform composition for further detailed studies.

We have also embarked on a study of electrolytes for solid-oxide fuel cells. This is motivated by the possibility of identifying materials that could lower the temperature needed to achieve a sufficiently high oxygen-ion conductivity. Both large scale (~MW) fuel cell systems operating at 800 – 1000 C and small scale (~W) thin film-based systems operating at ~500 C could use improved electrolytes. We prepare thin film composition spreads of oxides and fabricate hundreds or thousands of devices that are then characterized using impedance spectroscopy to infer the conductivity. In order to validate this approach we have studied the most well-known oxygen ion electrolyte, Zr1-xYxOy (yttria-stablized zirconia) using both parallel-plate and interdigitated electrode (IDE) configurations with Pt blocking electrodes. Model fits to the real and imaginary components of the frequency-dependent impedance are used to infer the ionic conductivity within grains. Validity of the model fits is challenging to assess, but a systematic approach was developed to vet fits for individual devices, allowing the conductivity to be inferred with reasonable confidence. We find that YSZ films processed at 500 C have intragrain ionic conductivities much smaller than bulk ceramics, and have a composition dependence that is also very different. YSZ films processed at much higher temperature, 850 C, yield results that substantially agree with those of bulk ceramics. We speculate that the high temperature anneal improves the degree of crystalline ordering, removing impediments to diffusion. We plan to use this synthesis/evaluation approach to identify new electrolytes, and have undertaken a study of the Zr- Sc-Y-O pseudoternary system. Thin films with compositions around Zr0.7Sc0.15Y0.15Oy processed at 500 C were found to have conductivities a hundredfold larger than Zr0.7Y0.3Oy films processed at the same temperature, suggesting an unexpected increase in local order with 1:1 Sc:Y incorporation. Further studies of this behavior are underway, as well as study of the properties of Zr-Sc-Y-O processed at elevated temperature, and the properties of other candidate oxide systems.

Prediction of Thermal Transport Properties of Multiscale-Structured Crystalline Materials

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Multiscale simulation has the exceptional capability to predict materials behavior from their chemical composition and microstructure. One most formidable obstacle standing in the way of progress in dynamic multiscale simulation in the past decade is the lack of a concurrent atomistic-continuum method that allows elastic waves, heat and defects to pass through the atomistic-continuum interface. As a consequence, waves will be scattered and defects will be reflected back by the artificial interface between different theoretical descriptions. This research aims to (1) establish a concurrently coupled atomistic-continuum methodology that can overcome this obstacle and can be used to optimize materials with microstructural complexity for desired properties and (2) demonstrate the methodology through predicting the mechanical and thermal transport properties of thermoelectric materials and comparing the predictions with experimental measurements.

In pursuit of this goal, the PI proposes to reformulate the classical statistical mechanical theory of transport processes so as to unify atomistic and continuum descriptions of balance laws and to recast the governing equations so as to facilitate coarse-scale finite element simulation of discontinuous materials behaviors. It is anticipated that this research will lead to (1) a new mechanical theory of transport processes that unifies atomistic and continuum mechanics, (2) a multiscale simulation tool that enables predictive simulation of materials behavior from the atomic to the macroscopic scale within a single theoretical framework, and (3) a fundamental understanding of the effect of microstructure, interfaces, and defects on phonon transport processes in complex thermoelectric materials.

Interfaces in Electronic and Structural Materials

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Many materials used in energy generation, conversion, storage and transmission are subject to high mechanical stresses pushing towards their theoretical strength and to high temperatures approaching the melting point. The ability of materials to function under such extreme conditions depends critically on their microstructure, primarily on thermal and mechanical properties of grain boundaries, twin boundaries and other internal interfaces. Creation and stabilization of optimum microstructure is key to achieving superior properties of many materials, ranging from high-temperature structural alloys for power generators, to contacts and conductor lines in integrated circuits and nano/micro electromechanical devices, to highly efficient thermoelectric materials. Development of revolutionary new materials for energy applications relies on fundamental knowledge of interfaces and our ability to design and control their properties.

The objective of the proposed research 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. These methods are capable of delivering critical atomic-level information about mechanisms of relevant processes and computing mechanical, thermodynamic and kinetic properties of interfaces. First principles calculations will also be performed for calibration of atomistic potentials and testing of key results. 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. Cu-Ag will be employed as a model binary system.

The research will be performed in collaboration with Dr. J. W. Cahn (NIST and University of Washington) on grain boundary migration and interface thermodynamics, and Dr. A. Karma (Northeastern University) on phase-field crystal simulations.

The project is expected to make a significant impact on the state of knowledge in interface science by improving the fundamental understanding of mechanical, thermal and dynamical properties of internal interfaces. It will also create a deeper understanding of intrinsic physical limits of interface properties under extreme mechanical and thermal conditions, and may suggest ways of approaching such limits in energy technologies. This goal is aligned with DOE's Grand Challenge of understanding and controlling matter in extreme environments.

Quantum Nanoplasmonics Theory

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Funding:	$143,000

This Program is in its initial period. It is directed toward development of novel and fundamental principles of quantum effects in nanoplasmonics. These are related to quantum behavior of both surface plasmons and underlying materials: metals, semiconductors, and dielectrics.

The first progress in this direction has been a prediction of a new effect: ultrafast metallization of dielectric nanofilms in strong optical fields (this is shared with another project supported by the AMOS Program). Another major direction of research in the framework of this project is the development of quantum theory of spaser (Surface Plasmon Amplification by Stimulated Emission of Radiation). Within this direction, we have shown that a metamaterial, in which a gain is introduced to compensate losses, will develop spasing causing saturation of gain that prevents the loss compensation.

In future research, we intend to develop theory of metallization of bulk dielectrics in strong optical fields. We will also participate in the ongoing experimental investigations of this class of phenomena in collaboration with the Max Plank Institute for Quantum Optics, Garching at Munich, Germany. We will also work on fully quantum-mechanical theory of spaser. Yet another direction will be quantum theory of high-harmonic generation in solid-state shells using nanoplasmonic concentration of optical energy. This will be a development of recent research.

Measurement of Near-Field Thermal Radiation Between Flat Surfaces with a Nanogap

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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. While recent works by other groups have demonstrated significant enhancement of nanoscale radiation, the sphere-plate arrangement can only allow an effective area to be around three square micrometers.

The method proposed here is to use ultrasmall gaps for measuring nanoscale radiation between flat surfaces with an area as large as one square centimeter. 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 educating students and future leaders in this area. Both fundamental advancement and experimental breakthrough are expected to result from this project. Understanding near-field thermal radiation is also related to the Casimir effect, which has important applications in microelectromechanical systems, nanotribology, and nanoscale devices.

Piezoelectric Nanogenerators for Self-Powered Nanosystems and Nanosensors

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The emerging development of nanotechnology today moves from inventing individual components to the integrated system that can perform one or more designed function by integrating a group of nanodevices with modern microelectronics technologies. A general integrated system is a package of components such as sensors, transducers, data processor, control unit, and communication system. As the size of the devices shrinks to the nano- or microscale, the power consumption also drops to a much lower level. Take a commercial Bluetooth headset as an example; its power consumption is just around several microwatts (data transmission rate ~500 kbits/s; power consumption 10 nW/bit). The power consumption of a nanodevice would be even smaller. At such a low power consumption level, it is entirely possible to drive the devices by scavenging energy from the sources in the environment such as gentle airflow, vibration, sonic wave, solar, chemical, and/or thermal energy.

We have been developing this “self-powered nanotechnology” since 2005, aiming at building a self-powered system that operates independently, sustainably, and wirelessly by itself without using a battery. Self-powered systems will play a very important role in the independent, sustainable, maintenance-free operations of implantable biosensors, remote and mobile environmental sensors, nanorobotics, microelectromechanical systems, and even portable/wearable personal electronics.

Mechanical energy in our living environment, for example, is abundant but irregular energy with variable frequency (mostly low frequencies) and magnitude, such as airflow, noises, human activity, which largely limits the application of the traditional resonator-based energy harvester that works at specific frequencies. A rational design is required to tolerate the variable environment. The nanogenerator (NG) using the piezoelectric effect of ZnO nanowires applies to such purposes. The NG relies on the piezoelectric potential generated in the nanowire as it is being dynamically strained under an extremely small force; a transient flow of electrons in an external load as driven by the piezopotential to balance the Fermi levels at the two contacts is the fundamental mechanism of the NG.

The power generated by a NG may not be sufficient to continuously drive a device, but an accumulation of charges generated over a period of time is sufficient to drive the device to work for a few seconds. This is very suitable for applications in the fields of sensing, infrastructure monitoring, and sensor networks. A common characteristic for these applications is that there are so many sensors in the system, and each sensor is expected to work independently and wirelessly, but all of them will be linked through a network/Internet.

In this project, we will try to demonstrate a prototype self-powered system that including an NG for harvesting mechanical energy, a low-loss full-wave bridge rectifier, a capacitor for storing the energy, an infrared photodetector, and a wireless data transmitter. The successful operation of this system will be the first proof of utilizing a NG for a self powered wireless sensor networks.

Amorphous Structures and Polymorphic Transitions in Metallic Glasses

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Phase-change multi-component chalcogenide materials, with $Ge_2Sb_2Te_5$ (GST) as a prototype alloy, are of strong interest 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 a-GST crystallizes on the time scale of ten 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. A thorough understanding of the atomic structure, chemical bonding, possible competing phases, phase relations and actual phase selections in the transforming a-GST is highly important to the science of phase-change materials. The new phases and their 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 project builds on our recent success and experience in uncovering the atomic-level structure and poly(a)morphism, but shifting 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 two-fold: (1) understand the atomic structure and the chemical bonding in the GST glass and (2) map out the phase relationships in the pressure (P)-temperature (T) space for GST. While the alloy remains amorphous, the atomic packing and electronic structures will be different in these various polyamorphs. We will explore the property (especially electrical resistivity variations) changes associated with the different densities and electronic structures. At the same time, 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.

Electric Field Effects in Liquid Crystals with Dielectric Dispersion

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Funding:	$180,000

We study dielectric response of liquid crystals to applied electric fields, in particular, dynamics of the director response. Currently we explore the electric-field induced changes in dynamics of fluctuations. The research is motivated by the fact that the recently claimed biaxial nematics demonstrate a uniaxial symmetry of order; and we attempt to explore whether application of the electric field can produce a biaxial order.

Diblock Copolymer Templated Two-Phase Inorganic Nano-Composites A Platform for Innovative Nano-Science

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Funding:	$127,000

Exciton semiconducting polymers are interesting and promising materials because of their fundamental physical properties and potential for photovoltaic applications utilizing the charges created by the controlled dissociation of photoinduced excitons. However, until now, coupling of exciton with magnetic and mechanical degrees of freedom has been elusive, although exciton magnetism is a well-known property. Here, we report for the first time on the observation of substantial visible light—electrically and mechanically induced changes of the magnetization of an organic exciton multiferroic consisting of single crystal P3HT doped with C60. An electric field of 5 MVm-1 switches the room temperature saturation magnetization on and off resulting in a magnetoelectric coupling coefficient of 40 mV/cm Oe at 100 Oe. Illumination of the composite with 615 nm light increases the room temperature magnetization about two fold. Stress changes the magnetization significantly more than that of crystalline metallic ferromagnets. The observations open new avenues for exciton based spintronic devices.

Electrochemically-Driven Phase Transitions in Battery Storage Compounds

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Funding:	$196,000

This project is a combined experimental and theoretical investigation of the effect of electrochemical driving force (applied electrical potential and current) on the phase transformation pathway in lithium intercalation compounds, including crystalline-crystalline and crystalline-amorphous transitions. During FY 2011, efforts were focused on understanding phase transition behavior in the mixed transition metal olivine, $Li(Mn,Fe)PO_4$. This system is of interest for several reasons. The end member $LiMnPO_4$ has a potential of 4.0V vs. Li/Li^+ compared to 3.45V for $LiFePO_4$, and therefore has substantially higher energy density as a battery cathode while not having so high a potential that special electrolytes are needed. However, the pure Mn end member has exceedingly slow charge-discharge kinetics which have prevented its commercial use. Interestingly, with even modest Fe additions, solid solutions $Li(Mn,Fe)PO_4$ when fabricated as nanoscale powders exhibit the highest power of all the simple lithium transition metal olivines, $LiFePO_4$ included. We regarded these as clues that important relationships between phase stability, phase transformation pathway, and external variables such as crystallite size and applied overpotential could be uncovered by studying this as a model system.

Available phase diagram data for this system shows three equilibrium crystalline phases as a function of Li content - the fully lithiated and fully delithiated end members, plus a phase of intermediate Li content. In-situ synchrotron X-ray diffraction experiments conducted at Brookhaven National Laboratory revealed that during electrochemical extraction (charging) and insertion discharging of lithium, metastable phase behavior abounds. During galvanostatic charging, an inherently low-overpotential process, amorphization rather than a crystalline-crystalline transition is typically seen. Only under high overpotential conditions, such as the end of galvanostatic charge, or under potentiostatic charge, does the equilibrium crystalline transition occur. Metastable solid solutions have also been observed during discharge. These results suggest that equilibrium phase assemblages are rarely attained under the dynamic real-world duty cycles to which automotive and stationary storage systems are subjected.

First Principles Determination of Structure, Thermodynamics, and Transport in Metals and Oxides

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First principles computation is slowly transforming fundamental materials science research. Starting from only basic information regarding the composition of a material it is now possible to predict many materials properties. This considerable progress in property prediction, as well as the emergence of some success stories in computational materials development, has made the potential for ab-initio computation as a virtual materials laboratory amply clear. In particular, in important technology areas such as energy storage and generation, where materials design needs to be accelerated significantly, computation is likely to play a crucial role. Limiting large-scale computational materials design is the lack of a predictive theory of structure. Hence, in this proposal we suggest a novel knowledge driven approach to predict the structure of materials with ab-initio methods, outline a strategy to investigate the role of electronic entropy in complex oxides at finite temperature, and plan to investigate the role of particle size on solid state phase transformations in materials. We believe that these are critical aspects of an ab-initio computational platform to accelerate the design of materials in energy generation and storage.

Near-field Thermal Radiation Between Two Objects at Extreme Separations

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Funding:	$159,000

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 an experiment will reveal interest phenomena when heat transfer transits from conduction to radiation. Experimental studies will be accompanied by theoretical investigations.

Surface Engineering by Simultaneous Action of Multiple External Fields

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Funding: $245,000

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. Our current research focuses on the surface morphological evolution and stability of electrically conducting (metallic) and semiconducting solids under the simultaneous application of mechanical stresses and electric fields. Special emphasis is placed on identifying the conditions under which the multiply driven surface morphology is stable and on exploring the complexity of the corresponding various morphologically stable surface patterns. In addition, we emphasize on 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 electric fields and mechanical stresses 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. The research focuses primarily on face-centered cubic (fcc) metals, such as Cu, and Si systems (bulk solids or substrates on which films or small islands can be grown epitaxially).

In terms of surface morphological response, the scope of the program is broad and includes the following research tasks.

(1) Continuum-scale analysis of morphological evolution and stability under surface electromigration conditions of (a) surfaces of stressed elastic solids; (b) surfaces of coherently strained thin films grown epitaxially on solid substrates; and (c) coherently strained islands grown epitaxially on solid substrate surfaces. In the case of heteroepitaxial systems, the analysis includes thick substrates, as well as thin deformable substrates that are either clamped onto holders or compliant.

(2) Atomic-scale analysis of surface morphological evolution, including fundamental studies on the role of strain relaxation mechanisms, such as plastic deformation dynamics, in (a) solids stressed beyond the linear elastic regime and up to their limit of strength; and (b) heteroepitaxial films/islands with thicknesses/sizes greater than the critical ones for misfit dislocation generation.

(3) Systematic studies of the effects of electromechanical conditions (varied over a broad range of material and operating parameters) on complex surface morphological response.

(4) Exploration of the synergistic or competing effects on surface morphological response of additional external fields, such as temperature gradients, applied to the solid-state materials of interest in conjunction with mechanical stresses and/or electric fields. These additional external fields also drive surface mass fluxes, e.g., due to surface thermomigration in response to imposed temperature gradients.

Domain Microstructures and Mechanisms for Large, Reversible and Anhysteretic Strain Behaviors in Phase Transforming Ferroelectric Materials

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In 2011, our computational studies focused on crystallographic domain engineering technique, correlated nucleation mechanism, poling-induced single-crystal-like piezoelectric properties of polycrystalline ceramics, and novel structures and functionalities of ferroelectric domain walls. Our previous study shows that self-accommodating lamellar domains provide optimal initial domain microstructures for field-induced inter-ferroelectric phase transformations to exploit desired piezoelectric behaviors with large, reversible and anhysteretic strain attributes. To fully exploit the potential of such behaviors, during this period of the project, we investigate the following issues: (1) How to control the domain configurations and sizes by crystallographic domain engineering technique? (2) What is the nucleation mechanism of crystallographic domain engineering? (3) How to engineer domains in polycrystalline ceramics? (4) What novel structures and functionalities do domain wall possess?

Our findings are summarized in the following:

(1) Crystallographic domain engineering technique for ferroelectric single crystals (published in *Applied Physics Letters* and featured as Cover Image): It is found that minimal domain sizes and highest domain wall densities can be obtained with appropriate combination of electric field magnitude, application direction along non-polar axis of ferroelectric single crystals, and temperature.

(2) Correlated nucleation and self-accommodating kinetic pathway of ferroelectric phase transformation (manuscript submitted): It is found that in order to circumvent insurmountable energy barrier of independent nucleation, ferroelectric nucleation exhibits strong spatial correlation and self-organization behaviors from the very beginning, and ferroelectric phase transformation proceeds via spatial and temporal evolution of self-accommodating domains that provide a low-energy kinetic pathway throughout the phase transformation process.

(3) Poling-induced single-crystal-like piezoelectric anisotropy in ferroelectric polycrystalline ceramics (manuscript under preparation): It is found that poling induces piezoelectric anisotropy in untextured ferroelectric polycrystalline ceramics with random grain orientations, and the maximum piezoelectric response of the poled ceramics is obtained along a macroscopically non-polar direction about 50 degrees away from the poling direction, resembling the anisotropy recently observed in ferroelectric single crystals.

(4) Novel structures and functionalities of ferroelectric domain walls (in progress): We have identified simple walls, complex walls, and wall arrays, demonstrated the capabilities of controlling the wall thickness and tuning the wall structure by external electric field, and continue to further investigate the novel functionalities of these domain walls and their potential technological applications.

Hetero-Junctions of Boron Nitride and Carbon Nanotubes: Synthesis and Characterization

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Hetero-junctions of boron nitride nanotubes (BNNTs) and carbon nanotubes (CNTs) are expected to have appealing properties that are not available from pure BNNTs and CNTs. The growth of BNNTs/CNTs junctions was hindered by the absent of a common growth technique for both types of nanotubes. Recently, we have succeeded for the first time to grow pure BNNTs directly on substrates. Since we have previously reported on the growth of CNTs by a similar technique, a common route for growing BNNTs and CNTs on substrates is thus obtained. Based on this unique capability, a thorough research plan is proposed here for exploring the basic growth mechanism and fundamental physical properties of BNNTs/CNTs junctions.

We aim to establish basic knowledge for growing these hetero-junctions with desirable segments of BNNTs and CNTs. Their structural, compositional, electronic, and photonic/optical, properties will be characterized. This project will enable the growth of desired BNNTs/CNTs junctions with tunable band structures and properties. Isolated and superlattices of these BNNTs/CNTs junctions are expected to have multiple functions, which is important for energy efficient device fabrications and applications. Every device fabricated from these junctions will be potentially useful for more than one type of application at a nanoscale. This project will also strengthen our collaboration with Oak Ridge National Laboratory (ORNL) through new user projects in the Center for Nanophase Materials Sciences (CNMS).

Understanding the Spin-Lattice Coupling in Multiferroic Oxides

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Temperature dependent (up to ~1100 K) studies of the local structure about the RE and Mn site in hexagonal $RMnO_3$ across the ferroelectric transition for R=Ho were. Shortening of the Ho-O bond was observed. Parallel temperature dependent x-ray diffraction measurements were conducted on $HoMnO_3$ over the range 300 K to 1400 K. An abrupt change in the x-ray pattern at 1350 K signals the onset of the high temperature paraelectric high symmetry structure. No abrupt changes in structure are observed on crossing the ferroelectric transition temperature near 875K. Detailed molecular dynamics simulations were conducted and reveal the nature of the structural changes coincident with the onset of ferroelecticity for the first time. Samples of orthorhombic $LuMnO_3$ and $HoMnO_3$ were synthesized by high pressure (3 GPa) and high temperature (1273 K) treatment of the corresponding hexagonal materials. The origin of the theoretically predicted high electrical polarization was probed. Infrared absorption (10 K to 300 K) revealed the onset of new phonons below 40K and as well as anomalous phonon hardening in the Lu system. Temperature dependent XAFS measurements of the Dy, Ho and Lu systems revealed large changes in the Mn-Mn and Mn-O-Mn correlation in the Lu system only, identifying the type of dynamic change responsible for the large polarization at low temperature. High pressure x-ray diffraction measurements were conducted on $DyMnO_3$ and $LuMnO_3$ over the pressure range 1 atm to 11 GPa (110,000 atm). The Lu system is found to have more isotropic ab plane compressibility. Application of pressure is found to enhance the electrical polarization and points to the use of strain as a parameter to tune the electrical polarization of these materials. These materials are predicted to be electronically driven ferroelectrics. The local a structure of $REMn_2O_5$ system was measured by x-ray and neutron total scattering (diffuse + Bragg scattering) pair distribution function (PDF) methods between 10 K and 300 K covering the magnetically ordered range (below ~ 45 K) with coupling between E and P. X-ray and neutron PDF measurements reveal the formation of nanoscale grains ~ 50 A at low temperature which lead to symmetry breaking. The nanoscale structures may play an important role in the observed low temperature polarization. The low energy lattice excitations (phonons) and magnetic excitation were also studied by inelastic neutron scattering. The full phonon spectrum is being explored.

Structure and Magnetism in Novel Group IV Element-Based Magnetic Materials

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The aim of 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 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 elucidating the nature and interplay between structure, chemical order, magnetism, and spin-dependent states in these novel materials, at developing materials and techniques to realize and control fully spin polarized states, and at exploring fundamental processes that stabilize the epitaxial magnetic nanostructures and control the electronic and magnetic states in these complex materials. Combinatorial approach provides the means for the systematic studies, and the complex nature of the work necessitates this approach.

We investigate phase decomposition of transition metal dopants in precipitation-free Ge DMS and its influence on ferromagnetic order, impurity states of transition metal dopants and their local environment in Ge DMS, electric field control of magnetic states in Ge DMS, structural and chemical ordering in Heusler alloys Co_2MnSi and Co_2MnGe, effects of composition and coherent epitaxial strain in Heusler alloys, spin dependent states that are responsible for electrical transport, and spin dependent transport through Si/Ge using these materials.

The research is a collaborative team effort between researchers and students at universities and national labs. It is leveraged against significant advances and resources in MBE synthesis of novel Si/Ge-based magnetic materials. Students are trained at many levels in areas of critical importance to future innovations in science and technology. The work promises to make significant impact on Si/Ge compatible spin-polarized materials by exploring and elucidating the fundamental processes that control structure, magnetism and spin polarization and by enhancing our ability to manipulate and tailor electronic and magnetic structures through atomic scale synthesis and characterization.

Bridging Atomistic and Continuum Scales in Phase-Field Modeling of Solid-Liquid Interface Dynamics and Coalescence

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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. 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 bicrystallography including the roles of solute and interfacial defects. The class of defects of particular interest include nanometer thin intergranular liquid films that reduce shear resistance and can lead to hot tearing during the late stages of solidification—a casting defect widely impacting the automotive and aerospace industries—and liquid inclusions that lead to stress concentration and failure in metallic and ceramic systems. 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. Through a collaborative effort, conventional phase-field and phase-field-crystal simulations are carried out jointly 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.

Magnetostructural Materials

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Magnetostructural transitions that are first-order in the Eherenfest sense comprise simultaneous magnetic and structural phase changes. Such transitions have the potential to deliver extremely large functional effects in response to small excursions in magnetic field, temperature, and strain. In this study, the effects of nanostructuring on magnetostructural transitions are of interest.

A phase-separated system of (FeRh)5Cu95 was synthesized via melt quenching under Ar atmosphere (wheel speed: 50 m/sec) with the goal of precipitating nanoscaled FeRh in a Cu matrix upon isochronal vacuum annealing for 30 minutes in the temperature range 100 K = T = 800 K. The magnetic and structural properties of the (FeRh)5Cu95 ribbons were compared with bulk FeRh which exhibits an abrupt antiferromagnetic - ferromagnetic transition accompanied by a unit cell volume change of 1% at T ~ 370 K. SQUID magnetometry, transmission electron microscopy (TEM) and X-ray diffraction (XRD) were used to determine the magnetic behavior and phases of the (FeRh)5Cu95 ribbons. While the annealed ribbons are a complex mixture of spin glass, ferromagnetic and paramagnetic phases, removal of the background Pauli paramagnetic susceptibility signal in the annealed ribbons reveals the presence of a magnetic phase transition at Tt = 130 K. This phase transition becomes more pronounced upon annealing at higher temperatures and is highly reminiscent of the bulk FeRh magnetostructural transition at 370 K. Additionally, thermal hysteresis in the transition has been confirmed in this system at low fields, consistent with the expected nucleation and growth signature of a first-order transition. Preliminary analysis indicates that this transition in the nanostructured material is more sensitive to magnetic field magnitudes than the bulk counterpart.

While XRD data indicate the presence of only Cu with a slightly expanded lattice parameter, TEM SAED imaging confirms the existence of coherent nanoscaled precipitates (~10-15 nm diameter) that are confirmed to consist of FeRh. These nanoparticles possess an orientational relationship with the Cu-rich matrix of the form: <110>Cu//<100>FeRh and {111}Cu//{011}FeRh.

If indeed the noted unusual magnetic response arises from the presence of FeRh nanoparticles, this result represents an unprecedented reduction in magnetic transition temperatures due to nanoscaling. Future research directions include experimental and computational investigations into the effects of elemental substitution on the transition, and investigation of the contribution of strain to the system. To enable a focused study of the effects of particle size on the observed magnetostructural transition, thin films of FeRh and MnBi, co-deposited with copper, silicon or alumina, are under development to synthesize, in a more controlled manner, nanoparticles with a designated range of sizes.

High Performance Nano-Crystalline Oxide Fuel Cell Materials: Defects, Structures, Interfaces, Transport, and Electrochemistry

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Funding: $500,000

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 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 viable, but for enabling new uses such as transportation and portable generation. SOCs can also be used to complement renewable sources by providing a means for storing energy as a chemical fuel such as hydrogen or methane.

This project aims to parlay our improving understanding of the enhanced electronic and ionic transport properties of nano-scale oxides and surfaces to address electrode performance and durability issues that limit the utility of SOCs. The scientific focus is on the dynamics of mixed nano- and micron-scale structures in SOCs at reduced operating temperature. New methods for fabrication and characterization of novel SOC materials are being developed.

The research encompasses air electrodes, fuel electrode, and electrolyte materials. Detailed investigations of the transport properties of various important oxygen ion conductor materials, in nano-crystalline form, have been carried out using novel analysis methods that allow separation of bulk and grain boundary components. The results help to disprove the notion, based on earlier reports, that such nano-scale materials can have much-improved ionic conductivities relative to micron-scale materials.

The electrochemical performance and stability of infiltrated air electrodes, such as $(Sm,Sr)CoO_3$ infiltrated into Gd-doped Ceria scaffolds, has been studied. Electrochemical and coarsening models have been combined to allow predictions of electrode long-term stability. The results suggest that desired polarization resistance and long-term stability can be designed into the cathode by choosing the appropriate infiltrate starting particle size and operating temperature. New nano-structures with improved stability have also been demonstrated.

We have also explored novel oxide fuel electrode materials where catalytic nano-particles nucleate during SOC operation and greatly enhance electrochemical kinetics. The dynamics of the nano-particle nucleation and coarsening processes are being studied both experimentally and by phase-field modeling. Recent results show that the electrode performance can be regenerated periodically.

Imaging Carrier Generation, Transport, and Collection in Nanostructured Materials

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The objective of our program is to develop a fundamental, quantitative understanding of light-induced carrier generation and transport between and within components of nanostructured materials to support the design and optimization of new materials for energy conversion. Raman spectroscopy and modeling is used to advance understanding of light absorption. Local optical excitation is also combined with electrical transport measurements of devices to spatially map carrier collection efficiency. In FY2011, we reported a major advance in each of these project thrusts.

PLASMONIC ENERGY HARVESTING

Semiconducting nanowires have been demonstrated as promising light harvesting units with enhanced absorption compared to bulk films of equivalent volume. However, for small diameter nanowires, the ultra-high aspect ratio constrains the absorption to be polarization-selective by responding primarily to the transverse magnetic (TM) light. While this effect is useful for polarization-sensitive optoelectronic devices, practical light-harvesting applications demand efficient light absorption in both TM and transverse electric (TE) light. In this study, we engineered the polarization sensitivity and charge carrier generation in a 50 nm Si nanowire by decorating the surface with plasmonic Au nanoparticles. Using scanning photocurrent microscopy (SPCM) with a tunable wavelength laser, we spatially and spectrally resolved the local enhancement in the TE photocurrent resulting from the plasmonic near-field response of individual nanoparticles and the broad-band enhancement due to surface-enhanced absorption. These results provide guidance to the development and optimization of nanowire-nanoparticle light-harvesting systems. (Spatially Resolved Plasmonically Enhanced Photocurrent from Au Nanoparticles on a Si Nanowire. Nano Letters 11, 2731 (2011)).

LIGHT-MATTER INTERACTIONS

The potential benefits of the nanowire geometry for the harvesting and collection of light are widely recognized, and very significant research efforts, in terms of both volume and impact, are being directed towards nanowire solar cells and photoelectrodes. We have advanced understanding of how light is absorbed in semiconductor nanowires as a function of their size and defect structure through detailed characterization by Raman spectroscopy coupled with finite difference time domain modeling of the response. The E^4 dependence of the Raman scattered light provides a stringent test of the accuracy of our model. The technique was applied to the discovery of new polytypes of silicon that are generated by the nanowire growth mechanism. Preliminary evidence of enhanced absorption and extended minority carrier diffusion lengths was observed. In addition, quantitative agreement between modeling and measurements of diameter dependent Raman scattering was achieved. (Silicon Nanowire Polytypes: Identification by Raman Spectroscopy, Generation Mechanism, and Misfit Strain in Homostructures. ACS Nano, ASAP (available on-line)).

Designing Nanoparticle/Nanowire Composites and Nanotree" Arrays as Electrodes for Efficient Dye-Sensitized Solar Cells"

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Funding:	$174,000

The objective of this proposal is to fabricate highly efficient photocathode dye-sensitized solar cells (p-DSCs) through the introduction of new nanostructured p-type semiconductors with proper valence band (VB) position, high visible transparency and high hole mobility. 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.

A major challenge in developing efficient p-DSCs is the lack of p-type wide-band-gap semiconductors. To the best of our knowledge, only NiO has been investigated for p-DSCs, which produce small photovoltage limited by its valence band edge position. Therefore, in this proposal, we will investigate Cu(I)-based p-type semiconductors such as $CuAlO_2$, CuSCN and CuI. Due to their lower valence band edge energies than that of NiO, we believe that p-DSCs with higher photovoltages and thus higher efficiencies can be fabricated. Such p-DSCs can be combined with the common n-DSCs for tandem solar cells with a theoretical efficiency limitation well beyond that of the single-absorber DSCs.

This renewal proposal will build on our prior establishments in the synthesis, electrochemistry and photoelectrochemistry of n-type semiconductor nanostructures for n-DSCs. The overall plan for carrying out this program includes (1) synthesizing nanostructured $CuAlO_2$, CuSCN and CuI, including nanoparticles and nanotubes; (2) investigating charge transport in the proposed p-type semiconductor films by both time-domain and frequency-domain techniques; (3) understanding the interfacial properties between the semiconductors and fluorine-doped SnO_2 (FTO) substrate (or other transparent conductors) in order to achieve the Ohmic contacts; (4) synthesizing dyes for p-DSC; and (5) measuring the energy conversion efficiency of our p-DSCs.

A major outcome of this project is that it will hold promise of fabricating more efficient p-DSCs than the current state-of-the-art ones, which will bring impact to the photovoltaic technologies. In a general sense, the proposed research program will bring progress in designing and synthesizing semiconductor materials at the nanoscale for energy-related application and establish an understanding of the electron transport process in these materials. The next phase of the study proposed here will include the integration of our p-DSCs with the n-DSCs for tandem DSCs with unprecedented high efficiencies.

Nanocrystal-Based Dyads for Solar to Electric Energy Conversion

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Funding:	$260,000

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. Of particular interest at the current time are the following:

(1) We are working to quantify the electronic energy level positions of the nanoparticles and their assemblies. Assemblies of CdSe nanoparticles (NPs) and CdTe NPs on a dithiol coated Au electrode were created, and their electronic energetics were characterized by using cyclic voltammetry in an electrochemical cell and by photoemission spectroscopy in vacuo.

(2) A major element of our effort is aimed at understanding how the solvation properties of the ligands, e.g., hydrophobicity and charge, can be manipulated to control the self-assembly of NPs into supramolecular structures and to arrange the NP-NP energetics in a way that facilitates charge transfer.

We are using ligand interactions to arrange different NPs in space and to manipulate the NP electronic states. We are exploring various aspects of how the ligand properties affect NP to NP charge transfer and NP to electrode charge transfer.

(3) We are developing computational methods to predict the properties of NPs. We have now completed the first systematic DFT (B3LYP/Lanl2dz approach) study of the structural and electronic properties of CdnSen/CdnTen nanoparticles (n=6, 9). Both bare and capped nanoparticles (NPs) with ligands coordinated to NP via amino, thio, and phosphinoxide groups were investigated.

Understanding and Design of Polymer Devices Interfaces

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Funding:	$342,000

This project builds on theoretical and experimental knowledge acquired with our previous grant and expands our multi-institution (Princeton University, Cornell University, Georgia Institute of Technology, and General Electric Global Research) collaborative research effort. The research pursued under this grant aims at (1) understanding the fundamental limits of engineering of polymer/electrode interfaces, in particular with respect to reducing carrier injection barriers; (2) devising new methods, including electrode surface modification and chemical doping, to circumvent the limitations on conventional barrier engineering; and (3) investigating the technique of physical lamination of polymer films as a new paradigm for building devices with independently optimized injection contacts and heterojunctions.

We combine state-of-the-art theoretical calculations (electronic structure), experimental techniques (spectroscopy of electronic states, interface chemistry, transport and injection measurements), device fabrication in an industrial context (light emitting diodes), and the proven track record for effective and productive collaboration. Optimization of polymer-based (opto)electronic structures, which ultimately depends on the complex interplay between charge carrier injection and transport, demands such a multi-directional approach.

The general outcome of the work is a new fundamental understanding of the electronic structure of polymer heterojunctions. In particular, this work has produced the first direct measurement of the molecular level alignment in a bulk heterojunction, i.e., in a film consisting of a blend of donor and acceptor materials, which constitutes the active layer of an organic solar cell. The work also produced a set of specific recommendations on the most effective methods to control charge injection barriers at these boundary regions. This work has direct impact on polymer-based lighting, electronics, and photovoltaic power conversion, and therefore contributes to an important mission relevant to DOE.

Architectural Photonics for Maximizing Solar Energy Conversion

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Funding: $250,000

The ultimate goal of solar-cell research is to achieve a near 100% solar-to-electricity conversion in a single junction on a cheap substrate. This task can be achieved if the entire sequence of light harnessing processes is optimized, including (1) 100% solar-collection efficiency, (2) 100% solar-absorption efficiency, (3) 100% internal quantum efficiency of a solar material (not discussed in this work), and (4) an infinitely narrow bandwidth of the solar spectrum. To accomplish this aggressive goal, limitations of photon-matter interactions set by fundamental, traditional optics must be overcome. Here, fundamental innovations are proposed based on an emerging modern optics—namely, sub-wavelength optics. In essence, an architectural network of sub-wavelength structure provides for a new degree of freedom to manipulate solar radiation that was not easily achievable by conventional optics.

Finally, the long-term scientific goal of this program is to achieve a solar-to-electric conversion efficiency of greater than 50% using a single photovoltaic (PV) cell. This study will elevate the technological efficiency gap, 45-100%, of solar conversion efficiency as of today. For comparison, the next generation PV cell design for efficiency close to 50% has as many as 127 MOCVD grown layers (courtesy: Fraunhofer Institute, Germany). The efficiency is also lower: ~28% for a single-crystal silicon photovoltaic cell and ~20% for any thin film cell.

Magnetic Frustration and Cooperative Phenomena in Correlated Electron Oxide Materials

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Funding: $135,000

Transition-metal oxides exhibit rich complexity in their fundamental physical properties determined by the intricate interplay between structural, electronic and magnetic degrees of freedom. While our prior work in this area was focused primarily on single crystal and bulk materials, the current project extends studies to low dimensional materials including thin films and nanocrystalline phases. Special attention would be given to exploring the role of dimensionality in transition-metal oxides through systematic experimental studies and establishing correlation between the structure, electronic and magnetic properties. In addition to continuing our studies further on the geometrically frustrated oxides identified in the past grant period, we propose extending studies of static and dynamic magnetic properties in new classes of topical oxides—mixed phase manganites ($La_{5/8}Pr_{3/8-x}Ca_xMnO_3$) with competing charge ordered and ferromagnetic phases strongly influenced by strain and low dimensionality; $Pr_{0.5}Sr_{0.5}MnO_3/Pr_{0.5}Sr_{0.5}CoO_3$ films and role of interface mediated effects on the phase diagram; AB_2O_4 type spinel ferrites that exhibit multiple spin re-orientation configurations and the $Ca_3Co_2O_6$ system which has Ising spin chains arranged on a triangular lattice geometry. All these systems are of current interest and have important unresolved issues that we intend to solve through our combination of DC, AC and RF magnetization studies coupled with neutron scattering and other local structural probes.

The proposed research will have a broad impact on understanding the physics in a large class of correlated electron materials—phase separated manganites, geometrically frustrated systems, spin ice materials etc., exhibiting correlation and disorder driven metal-insulator transitions, competing long range orders—as it addresses several key aspects that are common to many of these materials. Our continued synergistic collaboration between an academic institution and a DOE research laboratory would benefit undergraduate and graduate students, postdoctoral fellows and scientists involved in the research from both laboratories. Overall, the proposed project will advance knowledge and fundamental understanding of physics in an important class of complex oxide materials.

Energy Transport in Graphene

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Funding: $142,000

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 sp2 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.

These fundamental questions are currently being addressed using a comprehensive set of unique experimental techniques. Suspended micro-thermometers are being developed for measuring the temperature-dependent thermal conductivity of single-layer and few-layer, suspended and supported graphene flakes. Micro-Raman spectroscopy, infrared spectroscopy, and scanning thermal microscopy techniques will be combined for spatial mapping of temperatures of different energy carriers in externally heated as well as current-carrying graphene. These measurements are expected to lead to a detailed understating of energy transport in graphene.

Understanding Compound Phase Transitions in Heusler Alloy Giant Magnetocaloric Materials: Extension to Multifunctional Materials

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Our goal is to gain insight into the fundamental physics that is responsible for MCE and related properties at the atomic level. We are currently conducting a systematic study on the effects of atomic substitutions in Ni_2MnGa-based alloys, and also exploring related full- and half-Heusler alloys, for example Ni-Mn-X (X=In, Sn, Sb), that exhibit a wide variety of interesting and potentially useful physical phenomena. It is already known that the magnetocaloric effect in the Heusler alloys is fundamentally connected to other interesting phenomena such as shape-memory properties; and the large magnetic entropy change in $Ni_2Mn0.75Cu0.25Ga$ has been attributed to the coupling of the first-order, martensitic transition with the second-order ferromagnetic—paramagnetic (FM-PM) transition. Our research to this point has focused on understanding the fundamental physics at the origin of these complex, compound phase transitions, and the novel properties that emerge. The culmination of all of this work has revealed a scientifically interesting, and potentially quite useful, general theme: multifunctionality. The complex, compound phase transitions that are responsible for the large magnetocaloric effects observed in the Heusler alloys (and other materials) are also the origin of many other enhanced behaviors. These include giant magnetoresistance (GMR), magnetoelastic effects, bulk exchange bias effects, field-induced structural phase transitions, inverse magnetocaloric effects, and giant Hall effects. Even more interestingly, often two or more of these properties exist in the same material, making them prototypical multifunctional materials. One very exciting example is the class of materials that exhibit both “normal” and “inverse” magnetocaloric properties (i.e., both positive and negative magnetic entropy changes) near room temperature, spurring the development of a refrigeration cycle that exploits both types of effects. Our research objectives have therefore evolved to pursue not only magnetocaloric materials and the understanding of the underlying physics that dictates their behaviors, but also the multifunctional nature of the materials. This opens new vistas in which we may stumble upon new and exotic physics.

Nanophotonics-Enhanced Solar Cells

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The widespread use of photovoltaic (PV) cells for the production of renewable electricity is currently limited by their high cost and low efficiency. Advanced silicon and compound-semiconductor based PV cells achieve high power conversion efficiencies (PCE) (roughly 25 and 36%, respectively) but are too costly to produce and install. Organic PV (OPV) cells can be produced at much reduced cost, but the PCE of the best OPV cells is limited by optical absorption, resistive and other losses to values of approximately 6%. Here we propose to develop nanophonic approaches for PV cell efficiency enhancement. For OPV, these approaches have the potential of enhancing the efficiency to 40%. Our approach consists of:

(1) The integration of various organic PV subcells into highly efficient multijunction complexes. These architectures extract the maximum amount of useful energy from solar photon flux by minimizing loss processes that take place when a high-energy photon is absorbed in a low-gap semiconductor.

(2) The realization of highly conductive, yet transparent nanopatterned metal film contacts. The development of such films will solve a long-standing problem of stacked PV cells (where the current of the weakest cell limits the entire stack) by enabling efficient current extraction out of the side of the solar cell.

(3) The use of metal nanostructures as efficient antennas for capturing solar energy. These nanostructures will be used to optimize and tune the spectral response of the subcells to maximize the overall PCE. In addition, the nanostructures increase the subcell efficiency by improving energy coupling and transport within each subcell.

To accomplish the above goals, we have assembled an interdisciplinary team of experts in organic device engineering (Peumans), nanoscale device fabrication (Brongersma), nano-optics simulations (Fan) and optical (Brongersma) and electrical (Peumans) characterization.

Raman Spectroscopic Study of Coupling Between Magnetic and Ferroelectric Orders in Nanoscaled Thin Films Superlattices

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Funding: $150,000

(1) ATOMIC LAYER-BY-LAYER GROWTH BY LASER MBE FROM SEPARATE TARGETS

Most works of laser MBE use compound targets, such as a $SrTiO_3$ target to grow $SrTiO_3$ films. All elements in the oxide compound are ablated at once, and the film grows in a unit-cell-by-unit-cell manner. The approach lacks the stoichiometry control capability of reactive MBE with alternate monolayer growth. Homoepitaxial growth of $SrTiO_3$ on $SrTiO_3$ by laser MBE from $SrTiO_3$ targets frequently shows non-stoichiometry and lattice defects evidenced by a lattice expansion. In order to achieve atomic layer-by-layer growth, it is necessary to carry out laser MBE from separate oxide targets, for example growing $SrTiO_3$ from SrO and TiO_2 targets. The targets are switched back and forth to be ablated by the pulsed laser beam alternately, thus depositing one atomic layer at a time. The RHEED intensity recovers its original value when a complete $SrTiO_3$ layer is grown after the depositions of one SrO layer and one TiO_2 layer.

During FY 2011, we have investigated the homoepitaxial deposition of $SrTiO_3$ on $SrTiO_3$ substrate from SrO and TiO_2 targets and showed that by using separate oxide targets, laser MBE can achieve the same level of stoichiometry control as the reactive MBE. The first critical step for atomic layer-by-layer growth of oxide films is the preparation of atomically smooth single crystal substrates with specific surface termination. We have prepared TiO_2-terminated $SrTiO_3$ substrates for the homoepitaxial growth of $SrTiO_3$, and AFM images of treated $SrTiO_3$ substrates show stripes of steps with atomically smooth top surface; the height of each steps is about 0.4 nm, or one unit cell.

RHEED intensity for the (01) streaks along the [110] azimuth was monitored during the growth of $SrTiO_3$ films. The intensity reaches a maximum when one monolayer of SrO is deposited and decreases to a minimum when one monolayer of TiO_2 is deposited on top of it. The oscillation pattern with a stable RHEED intensity is characteristic of the Sr:Ti stoichiometry and full monolayer dosage for each layer. For the case of excess strontium, the RHEED intensity passes a peak before switching to the TiO_2 target. For the case of strontium deficiency, the ablation of the TiO_2 target starts before the RHEED intensity reaches a maximum; therefore, the peak maxima decrease in intensity over time. These characteristics were used to monitor and control the growth of the film in order to achieve desired stoichiometry and crystallinity.

The $SrTiO_3$ films of different stoichiometry were characterized by x-ray diffraction measurement. The result clearly shows that when the film is off stoichiometry, either Sr rich or Sr poor, the lattice expands. The further off stoichiometry is the film composition, the more the lattice expands. When the film has an exact 1:1 stoichiometry between Sr and Ti, however, the film peak overlaps with and is indistinguishable from that of the substrate. Around the film peaks, intensity oscillations are seen, which correspond to the film thickness and indicate smooth interfaces between the films and substrate. Again, when the film is stoichiometric, the oscillation is not visible because the deposited film and the substrate are indistinguishable from each other. The result is identical to that of atomic layer-by-layer growth of $SrTiO_3$ using reactive MBE. In the case of reactive MBE, the stoichiometry is controlled by adjusting the shutter open times for the Sr and Ti sources, aided by the RHEED intensity oscillation. For laser MBE, we control the stoichiometry by adjusting the numbers of laser pulses fired on the SrO and TiO_2 targets with the help of RHEED intensity oscillation. Both techniques have achieved equally excellent stoichiometry control.

(2) STRAIN RELAXATION IN $LaAlO_3$ FILMS AND ITS EFFECT ON THE 2D ELECTRON GAS AT $LaAlO_3/SrTiO_3$ INTERFACE

The remarkable existence of a high-mobility 2D electron gas (2DEG) at the interface between $LaAlO_3$ film and TiO_2-terminated $SrTiO_3$ substrate has generated significant interest. The origin of the conducting interface layer has been heatedly debated. The most dominant explanation attributes it to polar catastrophe due to the polar discontinuity at the $LaAlO_3/SrTiO_3$ interface, which causes a charge transfer of e/2 from the LaO^+ plane to the TiO_2 plane, giving rise to the 2DEG. A critical thickness of the $LaAlO_3$ film is needed so that the potential exceeds the bandgap. The effect of strain and strain relaxation should have significant influence on the 2DEG property as the polar distortions associated with the plane buckling in $LaAlO_3$ has been suggested to affect the electric potential in it.

$LaAlO_3$ films of different thicknesses were grown on TiO_2-terminated $SrTiO_3$ substrate by laser MBE from a $LaAlO_3$ target at 720°C. The $LaAlO_3$ films grow epitaxially with c-axis normal to the substrate surface. Grazing-incidence x-ray diffraction (GIXRD) was used to measure the in-plane lattice constant of films below 50 unit cells. For thicker films, the reciprocal space mapping (RSM) technique was used to characterize the epitaxial strain. For the GIXRD data, we found that no satisfactory fitting can be obtained if only one peak is assumed from the $LaAlO_3$ film, and two film peaks leads to good fit. For the thicker $LaAlO_3$ films, a broad double spot is found for the $LaAlO_3$ film. Both the two-peak fitting in GIXRD for thinner films and the double spot in RSM for thicker films suggest that there are two layers of different in-plane lattice constants in the $LaAlO_3$ films.

From the in-plane lattice constants of $LaAlO_3$ films as a function of film thickness obtained from both measurements, we see two in-plane lattice constants in $LaAlO_3$ films of all thicknesses, one is close to that of the $SrTiO_3$ substrate and the other decreases continuously when the film thickness is above about 20 unit cells towards the value of bulk $LaAlO_3$. A rough estimate using the areas under each peak in the GIXRD data reveals that the former layer is about 10 unit cells thick for all the $LaAlO_3$ films. A simple model to explain the result suggests that a thin $LaAlO_3$ layer of 10 unit cells next to the $SrTiO_3$ substrate is nearly coherently strained, while the top part of the $LaAlO_3$ film relaxes as the film thickness increases above 20 unit cells. When this occurs, cracks are seen in the films.

We have measured the sheet resistance R_s and carrier density n_s as functions of $LaAlO_3$ film thickness. For films thinner than 4 unit cells, the interface is insulating. Above 4 unit cells, both R_s and n_s are dependent on the $LaAlO_3$ film thickness. At about 20 unit cells, the same thickness when the strain in the $LaAlO_3$ film starts to relax quickly, R_s drops sharply and ns jumps by 2 orders of magnitude. Both remain relatively constant at larger film thickness. The value of ns below 20 unit cells is about $10^{14}/cm^2$, in agreement with about e/2 charge transfer at the interface.

MuSR Studies of Magnetic Semiconductors for Spintronics Applications

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Funding:	$210,000

The primary goal of this project is to investigate the internal magnetic fields in magnetic semiconductors that may have potential applications for spintronics. The main experimental technique is muon spin rotation (MuSR) in which 100% spin polarized positive muons are implanted into the material under investigation and serve as a very sensitive atomic scale probe of the local magnetic fields. The muon spin precession spectrum directly provides a measure of the local magnetic fields oriented perpendicular to the initial muon spin orientation. If the internal fields are well established in the ordered phase of a ferromagnetic (FM) material, that field is detected in the MuSR precession spectrum in zero applied magnetic field. A major part of this effort is zero-field MuSR measurements to determine whether the FM order is uniform throughout an order phase or very non-uniform, or whether the ferromagnetism is confined to a small volume of the sample. This is particularly important in diluted magnetic semiconductors, where the magnetism needs to be transferred from magnetic dopants to the charge carriers. We thus indirectly probe this transfer mechanism. We have detected Spin Polarons bound to the implanted muon in a number of magnetic semiconductors and in various strongly correlated materials. This is a quasi-particle in which a quasi-localized electron is exchange coupled to all of the ionic moments within the extent of its wave function. These ionic moments become aligned in a small FM bubble when the Spin Polaron is fully formed, independent of whether the exchange coupling with the responsible electron is positive or negative. We are investigating the extent to which small fully formed Spin Polarons exist in paramagnetic and/or AFM phases of numerous strongly correlated d and f electronic systems as a possibility for the quasi-particle responsible for a number of properties of these systems, including precursors to magnetic order, the origin of magnetoresistance, and as the source of magnetic interactions leading to superconductivity.

Structure-Optical-Thermal Relationships of Carbon Nanotubes

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The objective of this research is to develop a better understanding of phonon transport and coupled electron-phonon transport in graphene. As a two-dimensional (2-D) monatomic layer of sp2 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 are as follows.

(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.

These fundamental questions will be addressed using a comprehensive set of unique experimental techniques. Suspended micro-thermometers will be developed for measuring the temperature-dependent thermal conductivity of single-layer and few-layer, suspended and supported graphene flakes. Micro-Raman spectroscopy, infrared spectroscopy, and scanning thermal microscopy techniques will be combined for spatial mapping of temperatures of different energy carriers in externally heated as well as current-carrying graphene. These measurements are expected to lead to a detailed understating of energy transport in graphene.

Light Trapping, Absorption, and Solar Energy Harvesting by Artificial Materials

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Funding:	$135,000

We have demonstrated proof of principle in the design of photonic crystal based solar cells to dramatically improve (relative to any published structure) the overall absorption of sunlight in silicon-based solar cells using a three-section architecture consisting of less than 1 micron (equivalent bulk thickness) of silicon and no metallic mirrors. The three sections are (1) an anti-reflection (AR) layer consisting of a lattice of nano-cones placed on top of simple cubic photonic crystal, (2) the 3-D simple cubic photonic crystal (average rod diameter 170 nm and 350 nm lattice spacing) that traps light through a novel parallel-to-interface refraction (PIR) effect, and (3) a chirped photonic crystal back-reflector (BR) designed to absorb near-infrared light. Each rod contains a radial P-N junction and comprises an entire solar cell, with regions between the rods filled with silica (to mechanically protect the array) up to the tip of the nano-cones.

Our structure exhibits exceptionally good light absorption over a broad range of incident angles from 0° to 80°. This structure exhibits a maximum achievable photo-current density (MAPD) in the range of 27-30 milli-Amperes per square centimeter over the entire range of angles from 0° to 60°. Strategies to achieve and surpass the Shockley-Queisser power efficiency limit of roughly 33% are currently under investigation.

Coherent Control of Spin-States in Organic Electronics

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Funding: $185,000

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, therefore, the efficiency of light harvesting and light generating organic devices such as organic light emitting diodes and organic solar cells. Understanding these processes and understanding 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 and apply techniques which allow the quantum mechanical manipulation of spin states in organic semiconductor devices under device operating conditions. The influence of a quantum mechanical (so called coherent) control of device currents, 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 year, the work shifted towards the application of these techniques for the investigation of (1) organic light emitting diode (OLED) structures based on p-conjugated polymers [e.g., (poly-[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene (also called MEH-PPV)]; (2) diode devices based on Fullerenes [e.g., Phenyl-C60-Butyric-Acid-Methyl Ester (PCBM)], which are used as electron acceptor material in organic solar cells; as well as (3) mesoscopic organic/inorganic semiconductor heterostructures, which could be of great technological relevance for light harvesting in third generation (nano-structure based) solar cells technologies.

The results of these efforts have revealed a number of important insights. The study of polymer light emitting diodes has led to the identification of two controversially discussed recombination (=charge carrier- and energy-loss) mechanisms: (1) the so called polaron pair recombination mechanism and (2) the triplet-polaron quenching mechanism. Previous studies by other research groups remained inconclusive on which of these two processes would be present in the investigated material. Our results revealed that both mechanisms can occur in the same material.

Our study of heteromaterials focused on spin-dependent processes in nanoscale Cadmiumselenide (CdSe)/Cadmiumsulfide (CdS)-tetrapod structures whose surfaces where coated with organic ligand molecules. In these mesoscopic structures, light harvesting takes place by absoption of light in the rod-like shaped CdS domain. Our experiments revealed that photogenerated charge carriers will eventually be transferred into the CdSe domain. However, before this transfer takes place, one charge carrier species (electrons or holes) separates from the other charge carrier species for comparatively long amounts of time (order of microseconds) into localized states on the organic ligand molecules. The transfer of both charge carriers of a pair into the CdSe domain is then controlled by the pair’s spin orientation in the separated state.

Fundamental Studies of Unconventional Sulfide Semiconductors for Cost- Effective and Environmentally Benign Thin Film Photovoltaics

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Funding:	$300,000

This SISGR project is aimed at determining some of the fundamental properties of semiconductors which are composed of commodity elements, especially sulfur, in order to enable the scale-up of terrestrial thin film photovoltaics to TWP levels.

In one branch of our investigations, we investigate the materials combinations that should result in charge separating heterojunctions using such unconventional materials. To this end, we are calculating the band offsets of heterojunctions of candidate materials, satisfying the standard bandgap and optical absorption criteria to identify pairs with favorable band alignments. We are also extending this investigation to the defective limit in which the Fermi level is pinned in the bulk, as will result from low-cost, low-temperature processing. In these cases, Type II band offsets are desirable as the band bending usually relied upon to allow tunneling through interface barriers is not possible.

In the experimental branch of our investigations, we focus on the growth of Cu_2ZnSnS_4 (CZTS) using magnetron sputtering followed by rapid thermal processing and on the characterization of phase and point defects in CZT(S,Se) films. These defects are expected to limit the performance of solar cells using CZT(S,Se) as absorber layers; however, there is very little known about their identity of quantitative effects to date. We use advanced I-V and C-V techniques to measure the signatures of these defects and are working to correlate their numbers and electronic states with material properties such as photocarrier lifetime as well as device performance.

Thermodynamic and Kinetic Studies of High Temperature Proton Conductors (HTPC) Using Thin Films and Porous Bodies

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Funding:	$158,000

The objective of the work is to examine transport through mixed proton, oxygen ion, and electron (hole) conductors. These materials are candidates for application as fuel cells, electrolyzers, electrochemical reactors, oxygen, and hydrogen separators. The transport is electrochemically coupled. We have analyzed transport through such materials using Onsager formulation. It is shown that ionic and electronic transport is coupled. Coupling of transport also affects transport pheneomena involving multiple phases. For example, degradation of PEM fuel cell cathodes occurs by the growth of Pt catalyst particles. A generic mechanism applicable to electrochemical Ostwald ripening and/or agglomeration of metallic particles immersed in requisite salt solutions is proposed. The model was verified on copper powder immersed in $Cu(NO_3)_2$ salt solutions. These results demonstrate that in PEM fuel cells, cathode degradation is expected to be much greater than anode degradation, consistent with experimental observations. A paper based on this work was published in the *Journal of Electrochemical Society*.

In any practical fuel cell, significant losses occur in current collection. Typical geometries used are either planar or tubular. It is known that the temperature dependence of fuel cell performance is different for planar and tubular cells. We conducted a detailed analysis of current collection in tubular fuel cells. In tubular cells, the sheet resistance (which exhibits metallic conduction) may completely dominate net resistance at high temperature, leading to this peculiar behavior. A paper based on this work was published in the *Journal of Power Sources*.

A theoretical model has been developed, based on linear non-equilibrium thermodynamics, that describes degradation of Lithium ion batteries. The paper reference is, "A model for degradation of electrochemical devices based on linear non-equilibrium thermodynamics and its application to lithium ion batteries," A. V. Virkar, J. Power Sources, 196 (14) 5970-5984 (2011). Studies on the measurement and analysis of porous ionic conductors were conducted on Sm_2O_3-doped ceria. The paper reference is, "Conductivity of porous Sm_2O_3-doped CeO_2 as a function of temperature and oxygen partial pressure," J. Wright and A. V. Virkar, J. Power Sources, 15 (1) 6118-6124 (2011). Three invited talks have been given in 2011: ECS meeting, MS&T meeting, and MRS meeting.

Towards Quantitative Understanding of Strain Induced Nanoscale Self-Assembly from Atomic-Scale Surface Energetics and Kinetics

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The main objective of this theoretical/computational research project is to achieve a better fundamental understanding of stress (strain) effect on physical behaviors of materials. Specifically, we will focus on two topics: (1) 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. We will employ a multi-scale approach, combining several state-of-the-art theoretical and computational techniques, ranging from density-functional-theory based first-principles electronic structure calculations to continuum 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. In the second topic, extensive first-principles electronic structure and stress calculations will be carried out to reveal a novel quantum stress effect, which has an electronic origin rather than the classical stress effect originated from atomic and lattice size difference. We will focus on quantum stress effects induced by doping of semiconductors and quantum stress induced phase transitions. The general concept of quantum stress is expected to have broad implications in many other systems.

Elucidation of Hydride Interaction Mechanisms with Carbon Nanostructures and the Formation of Novel Nanocomposites

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Funding:	$75,000

The objectives of the theoretical work are to provide a fundamental understanding of the interaction of hydrogen with metal clusters and how it is affected when they are embedded in carbon nano-tubes and fullerenes, as well as to guide experiments in the discovery of new materials suitable for hydrogen storage with high gravimetric and volumetric density. It is well known that metal clusters possess unique properties that are very different from their bulk. In addition, these properties can be tailored by changing the size, shape, composition, and charge state—one atom and one electron at a time. Since metal clusters embedded inside a carbon nano-tube can interact with the tube through charge transfer, it will be important to understand how the charge on a bare cluster affects the strength of binding of hydrogen. We had demonstrated some time ago that a Ni cation can bind to as many as six hydrogen molecules while the neutral atom can only bind two hydrogen atoms. In addition, the hydrogen atoms were bound to the cation in molecular form with binding energies of the order of a few tenths of an eV while they bind dissociatively to the neutral atom. The focus of our study is to use metal centers embedded in carbon-based materials to trap hydrogen in molecular form so that they can be desorbed under ambient thermodynamic conditions.

Mesoscale Interfacial Dynamics in Metnetoelectric Nanocomposites

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$217,000

OVERVIEW AND PROBLEM DESCRIPTION

Multiferroic materials have a coexistence of at least two ferroic orders (ferroelectric, ferromagnetic, or ferroelastic). In multiferroic materials, the coupling interaction between the different order parameters can produce new phenomena, such as the magnetoelectric (ME) effect. The ME response is the appearance of an electric polarization P upon applying a magnetic field H, and/or the appearance of a magnetization M upon applying an electric field E. Magnetoelectricity has been observed as an intrinsic effect in some natural materials at low temperature; however, such single phase materials suffer from extremely weak ME exchange. Better alternatives are two-phase composites consisting of magnetostrictive and piezoelectric phases, which have been shown to have large ME coefficients. Said composites exploit a unique product ME tensor property that depends upon the individual strictions of the piezoelectric and magnetostrictive phases, the elastic stiffness and integrity of the interphase interfaces, the phase distribution and the dimensionality of its connectivity, and any elastic constraint, amongst other things. This is further complicated by the fact that the symmetry of the individual phases can be altered by epitaxy and the crystallographic direction along which that constraint is applied. Accordingly, two-phase heterogeneous oxide systems are unique in that both the nanostructure and the crystal structure can be engineered by an integrated approach, offering richness in symmetry and meso-scale texture that has yet to be fully exploited. This research program between Virginia Tech [D. Viehland (PI) and S. Priya] and Rutgers University (A. Khachaturyan) proposes to investigate the mesoscale physics and chemistry of such two-phase ME layers and to use epitaxial engineering of nanostructures and crystal structures to realize polarization-magnetization coupling of unique product symmetries.

SPECIFIC OBJECTIVES OF THE PROGRAM

Objective 1: Develop two-phase magnetostrictive/piezoelectric nanocomposites having near-periodic nanostructures. Fine nanowires with a chessboard-like morphology will be grown by an eptiaxial engineering approach, and the influence of interphase-interface density on the ME exchange will be investigated.

Objective 2: Develop a synthesis process for confining the effects of composition/strain gradients across only the interface and inducing interfacial chemical reactions. The new nano-chemistry at the interface will be used to actively tune the elastic compliance mismatch. The approach will allow the design and synthesis of interphase interfaces with varying spatial connectivities, enabling optimization of the interface dimensionality and geometry that not only maximizes the elastic strain transfer but also minimizes demagnetizing fields.

Objective 3: Develop a 3-D Phase Field model of spontaneously self-organizing nano-scale microstructures driven by composite chemistry, microelasticity, magnetism, and/or ferroelectricity, predicting their responses to electric, magnetic, and stress fields.

Optical Properties of Doped ZnO Nanocrystals and Ceramics

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Students:	0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$151,000

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 program utilizes 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 is investigated from the nanometer to micron 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:

- Determine the microscopic structure of H complexes in ZnO nanocrystals.
- Investigate the effect of particle size on dopant concentration and charge state.
- Probe H and Cu energy levels as a function of quantum confinement, alloying, and pressure.
- Investigate the effect of Cu doping on the optical properties of ZnO nanocrystals and ceramics.
- Achieve p-type doping of ZnO nanocrystals.

Optical spectroscopy, performed at Washington State University (WSU) and University of Idaho (UI), is complemented by work at DOE user facilities at Pacific Northwest National Laboratory (PNNL) and Lawrence Berkeley National Laboratory (LBNL).

In Situ NMR Studies of Hydrogen Storage Systems

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	Majzoub, Eric, MISSOURI, UNIVERSITY OF
Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding:	$190,000

A key feature of complex hydrides for their use in hydrogen storage is that there are at least two metal atoms which phase-segregate upon dehydriding. To rehydride the material (by adding H_2 gas), there must be some mechanism to transport the separated metal atoms to bring them back into intimate, atomic-level contact with each other. We have recently discovered a mobile, aluminum-bearing species in the chemistry of $NaAlH_4$, the archetype of complex hydrides. This mobile species is a vacancy-ridden form of $NaAlH_4$ and is likely a key intermediate in the chemistry of this material. The current project aims to extend that work and find related mobile species in other complex hydride materials, such as $KAlH_4$, Na_3AlH_6, and the borohydrides. In particular, the borohydrides offer large mass fractions of hydrogen, so they are particularly attractive for storage applications. In situ NMR will be used, with the NMR taking place at the high-temperature and high-pressure conditions of the hydrogen reactions.

The simplest ionic hydride, NaH, will also be examined. By using the deuterided analog, NaD, we will employ deuterium NMR and its sensitivity to electric quadrupole interactions to distinguish D atoms that are not at sites of high symmetry. These are D atoms near vacancies and heteroatom defects. The aim is to identify the defects that are responsible for H(D) transport and measure the rate of hopping motion by slow-motion techniques on the D atoms that are neighbors of the defects.

Characterization of High Density/High Stability Glasses

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Sr. Investigator(s):	
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Funding:	$146,000

We have recently discovered that organic glasses with high density, low enthalpy, and extraordinarily high kinetic stability can be prepared by physical vapor deposition. Prior to our work, these high density/high stability glasses would have been considered to be “impossible materials” in that one would have to age an ordinary glass for thousands of years or more to achieve similar properties. In order to reveal the full potential of these stable vapor-deposited glasses for a variety of applications, and to answer fundamental questions about the amorphous state, we are working to achieve the following objectives:

(1) Prepare stable glasses via vapor deposition from a wide range of materials. We have successfully prepared stable glasses from four isomers in the trisnaphthylbenzene family. Given that stable glass formation occurs for systems with drastically different glass transition temperatures and glassforming ability, we conclude that stable glass formation is a general phenomenon when the correct deposition conditions are utilized.

(2) Characterize the local packing in stable organic glasses using wide-angle x-ray scattering. These experiments show evidence for anisotropic packing in highly stable glasses. This anisotropy may lead to higher charge mobilities in the glasses that are utilized in organic electronics.

(3) Measure density changes of stable glasses during thermal cycling with spectroscopic ellipsometry. These experiments show that highly stable glasses can be birefringent, can have densities that exceed those of ordinary glasses by more than 1.2%, and have a lower thermal expansion coefficient than ordinary glasses. In addition, the ellipsometry experiment provides access to kinetic stability.

(4) Understand how the mechanical properties of glasses can be controlled by vapor deposition. Brillouin light scattering has been used in conjunction with a temperature gradient deposition stage to obtain the moduli of vapor-deposited glasses of indomethacin over a wide range of substrate temperatures. The modulus can be controlled over a 30% range in this manner. These results confirm that vapor-deposited glasses provide a new palette of materials for fundamental research that may also influence future technologies.

DOE National Laboratories

Complex Hydrides - A New Frontier for Future Energy Application

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Students:	2 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$545,000

The purpose of the integrated experimental and modeling effort is to achieve a fundamental understanding of the relationships between the chemical composition, bonding, structure, microstructure, properties, and performance of novel hydrogen-rich solids, and as a result, develop predictive tools to enable guided discovery of materials at the atomic scale and controlling processing strategies at the nano-, meso- and microscopic scales. This research is being carried out by a multidisciplinary team of scientists from the Division of Material Science and Engineering Programs and Chemical and Biological Sciences Programs in collaboration with Physics Department at Virginia Commonwealth University. A number of experimental (Ames Laboratory team) and theoretical (Virginia Commonwealth University team) approaches are brought to bear on a variety of complex metal hydrides in order not only to achieve controlled dehydrogenation, but also to accomplish full rehydrogenation and long cycle life of extremely hydrogen rich solids to meet US DOE goals of volumetric and gravimetric hydrogen capacity. We attain this through basic knowledge of transformation mechanisms in complex hydrides-hydrogen systems, thus precipitating discoveries needed for future transition to hydrogen – a renewable, clean, and safe energy carrier.

Extraordinary Resp. Magnetic Rare Earth Materials

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Sr. Investigator(s):	Gscheidner, Karl, AMES LABORATORY Miller, Gordon, AMES LABORATORY Chumbley, L. Scott, AMES LABORATORY
Students:	3 Postdoctoral Fellow(s), 2 Graduate(s), 2 Undergraduate(s)
Funding:	$1,161,000

Integrated experimental and theoretical investigations of complex metallic systems where, as a result of a small change of an external stimulus, such as temperature, pressure, or magnetic field, the material responds with an intrinsic phase change. This leads to a drastic variation of the majority, if not, all of the physical properties of a material. Model systems under study include intermetallic compounds containing rare earth metals (R) such as Gd, Tb, Dy, etc., main group elements (T) such as Si, Ge, Ga, etc., and transition metals such as Fe, Co, and Ni. We focus on a wide range of stoichiometries, including R_5T_4, RCo_2, RNi, $(R1\text{-}xR'x)Al_2$, and $La(Fe1\text{-}xSix)_{13}$ compounds. Common to different model systems are potent changes of the electronic transport behavior (e.g., electrical resistance), shape (e.g., temperature or magnetic field induced strain), and thermodynamic properties (e.g., strong thermal effects), thus highlighting commonalities related to strong coupling of crystallographic and electronic degrees of freedom that span across different families of materials. Our main goal is to uncover the underlying electronic, atomic and microscopic interactions that result in an extraordinarily strong coupling of the electronic (magnetic) and crystal lattices, and therefore, in extensive changes of their atomic and electronic structures, and all derivative properties in these rare earth-based materials. In order to achieve predictive power (and in the future to facilitate the creation of functional materials by design rather than by serendipity) we are developing and validating phenomenological models of transformations that range from magneto-volume to magnetic-martensitic, which is another prime objective of this research.

Proximity Effects in Conducting Oxide Heterostructures

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Highland, Matt, ARGONNE NATIONAL LABORATORY
Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $1,313,000

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. Proximity effects associated with charged interfaces are amplified when heterostructure layer spacings are reduced below distances where the charges at neighboring interfaces strongly interact. 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 model heterostructures we create are based on fluorite- or perovskite-structured materials. Growth techniques that enable precise control of each atomic plane in a growing heterostructure of these materials are employed, including new capabilities in sputter deposition and atomic layer deposition. X-ray characterization of interfacial structure/chemistry, strain/composition gradients, and defect behavior is combined with in-situ electrical characterization to provide unique insight into structure-property relationships. The program integrates experimental measurements with a theoretical effort that uses firstprinciples calculations to elucidate the factors that control growth behavior and properties.

Superconducting Materials

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$714,000

This program investigates the basic relationships between nanostructures and the macroscopic properties of superconductors. During FY 2011, significant progress was made. A selected few are listed below:

(1) We found unusual persistence of superconductivity against high magnetic fields in the strongly-correlated iron-chalcogenide film FeTe:Ox - Below 2.52 K. Instead of saturating like a mean-field behavior with a single order parameter, the measured low-temperature upper critical field increases progressively, suggesting a large supply of superconducting states accessible via magnetic field or low-energy thermal fluctuations. We demonstrate that superconducting states of finite momenta can be realized within the conventional theory, despite its questionable applicability. Our findings reveal a fundamental characteristic of superconductivity and electronic structure in the iron-based superconductors.

(2) More than 30% Tc enhancement has been achieved in superconducting FeSe0.5Te0.5 thin films by CeO_2 buffer layer - High quality FeSe0.5Te0.5 thin films have been made on various substrates, such as $SrTiO_3$, $LaAlO_3$ and YSZ, and some with CeO_2 buffer layers. Superconducting transition temperature Tc as high as 20K was obtained, this is more than 30% increase over that of the bulk samples (~15K). It was found that CeO_2 buffer layer not only increases Tc, but also greatly enhances the critical current density Jc, and over 2 MA/cm^2 of Jc at liquid helium temperature has been obtained in these CeO_2 buffered FeSe0.5Te0.5 thin films.

(3) Possible coexistence of superconductivity and ferromagnetism in K0.8Fe1.6+xSe2 single crystals was probed – We found an unusual peak in the resistivity in a layered iron-chalcogenide K0.8Fe1.6+xSe2 single crystal when the electrical current is applied perpendicular to the ab planes, which coincides with the onset of increasing magnetic moment and a second order phase transition in the H-T plane, as determined in magnetization and specific heat measurements. The emergent H-T phase diagram, in conjunction with the structural analysis with TEM and local chemical probes (EDX), suggest that there is a possible coexistence between superconducting and ferromagnetic domains.

(4) Evidence of large structural disorder in the superconductor K0.8Fe1.6+xSe2 was found - The local structure was studied by x-ray absorption spectroscopy and high resolution TEM. Near-edge spectra reveal that the average valence of Fe is 2+. The structure about the Se and Fe sites shows a high degree of order in the nearest neighbor Fe-Se bonds. On the other hand, the combined Se and K local structure measurements reveal a very high level of structural disorder in the K layers. Temperature dependent measurements at the Fe sites show that the Fe-Se atomic correlation follows that of the Fe-As correlation in the superconductor LaFeAsO0.89F0.11 - having the same effective Einstein temperature (stiffness). In K0.8Fe1.6+xSe2, the nearest neighbor Fe-Fe bonds has a lower Einstein temperature and higher structural disorder than in LaFeAsO0.89F0.11. The moderate Fe site and high K site structural disorder is consistent with the high normal state resistivity seen in this class of materials. For higher

shells, an enhancement of the second nearest neighbor Fe-Fe interaction is found just below Tc and suggests that correlations between Fe magnetic ion pairs beyond the first neighbor are important in models of magnetic order and superconductivity in these materials.

Structural and Electrostatic Effects in Self Assembled Nanostructure Growth

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

This year has been a transition period between the previous single investigator FWP, focusing most recently on nanoparticles, and the (hopefully) future, multi-investigator FWP focusing on materials for nuclear energy applications. Among the completion goals for FY 2011 were the publication of three articles, preferable in high impact journals. On article, “CuO Nanobarrells” has been accepted for publication in the November/December issue of the admittedly non-high impact Journal for Science and Technology. A second paper, “The effect of size for nanoparticle dissolution” has been reviewed by ACS Nano, and currently is under discussion by us (the authors Farrell, Ginosar, Petkovic, Parra and Van Siclen) and the Editor. The third paper has undergone several sea changes; we (Farrell, Ginosar and Petkovik) formed a collaboration with Millie Dresselhaus and a former gradient student of hers, Xiaoting Jia, to include some of their experimental results. This then led to the subsequent inclusion of several of their collaborators and too many ideas to include in one paper. As a consequence we are deconstructing the current manuscript down into two articles that we still intend to publish in a high impact journal.

Talks that have been given on this work include “CuO Nanobarrels” at the annual Physical Electronics Conference in San Diego, CA, in January, 2011, and a more general talk titled “A Universal Model for Nanoparticle Size Effects” that encompasses the last several years work and has been given at Idaho National Laboratory, Idaho State University, City College of New York, and DePaul University. Talks are also planned for Ohio State University, and probably the University of Cinncinnati, the University of California at Santa Barbara, and several other institutions. It should be noted that while these talks technically extend beyond the FY2011 fiscal year, they have been undertaken with the intent to publicize the work done on the previous FWP as a complete body where the totality is greater than the sum of the parts. A poster presentation on the previous funding cycles work was given at the BES Contractors Meeting held at Airlee House in Virginia in May, 2011.

Characterization of Functional Nanomachines

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Students:	1 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$940,000

This project establishes a multidisciplinary team at LBNL to develop, characterize, and better understand the fundamental behavior of mechanical structures at the nanoscale. Two paths will be followed toward this goal: (1) naturally occurring bio-motors will be harnessed to take advantage of the molecular mechanisms provided by Nature, and (2) new synthetic molecular machines will be designed in a molecule-by-molecule fashion. The first direction involves exploring chemically engineered molecular structures, purposefully designed with specific mechanical functions in mind. The second involves exploitation of the unique mechanical properties of graphene and nanotube-based nanostructures to create novel, nanomechanical devices. A common theme is to explore the fundamental mechanical response of nanostructures to external forces (such as pressure or electromagnetic stimulus) and internal changes (such as phase transitions and chemical reactions) and to clarify the basic mechanisms by which they convert energy from one form to another. These efforts will help form the scientific foundation underlying new molecular-mechanical nanotechnology with applications in areas of importance to DOE including chemical and photo-sensing, computation, power generation, and active surface control.

Electronic Materials Programs

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Students:	0 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding:	$1,451,000

The goal of the Electronic Materials Program is 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. Progress in these areas is essential for the performance and reliability of a number of technologies that lie at the heart of the DOE mission, including solar power conversion devices, solid state sources of visible light, visual displays, and a large variety of sensors and power control systems for energy generation, conservation, distribution and use.

The Electronic Materials program additionally received at least half of the research effort of two postdoctoral fellows and seven graduate students who were supported by outside sources (fellowship, TAship, etc).

Nanocomposite Proton Conductor

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Students:	3 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$850,000

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 (NMR). First-principles methods are developed to provide a general basis for computer-aided materials design of ABO_4 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.

Nanomaterials and Bioinspired Approaches to Solar Derived Fuels

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Sr. Investigator(s):	
Students:	15 Postdoctoral Fellow(s), 14 Graduate(s), 0 Undergraduate(s)
Funding:	$2,336,000

Scientists at the Helios Solar Energy Research Center (SERC) of Lawrence Berkeley National Laboratory are developing solar-driven chemical converters that will create transportation fuels from water and carbon dioxide, in a process that doesn’t rely on either biomass precursors or the availability of arable land. Centered at Berkeley Lab and led by Dr. A. Paul Alivisatos, this project also includes experts from UC Berkeley and several other universities. Research focuses on advanced nanomaterials for use in solar light collectors and electrodes, a new generation of catalysts for energy-efficient chemistry, and specialized soft and hard membranes for integrating the light harvesting, charge separating and fuel forming components. The Helios SERC goal is to develop a process that takes place on a single nano-material platform and uses abundant and non-toxic materials and inexpensive manufacturing processes; these requirements will allow the process to be scaled to a size that will significantly reduce the need for fossil fuels in transportation. Forty scientists from the fields of chemistry, materials sciences, physics, biology, and engineering are working together to accomplish this ambitious project. Overcoming the basic science challenges of this goal comprises the work of three team efforts: Components, Integrated Systems, and Crosscutting Science.

Nanostructured Materials for Thermoelectric Energy Conversion

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Ramesh, Ramamoorthy, LAWRENCE BERKELEY NATIONAL LAB
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Urban, Jeffrey, LAWRENCE BERKELEY NATIONAL LAB
Students: 2 Postdoctoral Fellow(s), 5 Graduate(s), 0 Undergraduate(s)
Funding: $740,000

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, $ZT = S2sT/k$, where S is the thermopower or Seebeck coefficient, and s and k 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.

Spin Polarized Functionality through Complex Oxide Heteroepitaxy

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Principal Investigator: Suzuki, Yuri
Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: $250,000

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 and 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 Design, Physics and Applications

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Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$650,000

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, an impressive progress has been made in the field, covering a wide variety of exotic optical properties. One of the most exciting properties of metamaterials is their ability to image object beyond the diffraction limit. The quest for the perfect lens initiated and inspired the research in the field of metamaterials and has driven the field for many years. Being able to have in the far field a perfect image of an object is the dream in many physics and technology research. We have already demonstrated considerable steps toward this goal and believe that the physics and technological aspects to be revealed in this project will bring a practical solution to real-time sub-diffraction imaging in far field and will have revolutionary applications in fields ranging from optical communication to energy harvesting.

Electronic Processes

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Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$441,000

The central goal of this program is to advance our understanding of organic electronic materials and to uncover the underlying physical principles that dictate their performance in existing and novel electronic devices including: organic light emitting diodes for display and lighting applications, organic field effect transistors for large area electrical drive circuits, and organic optical detectors and solar cells. These materials continue to be of great scientific interest because of their rich, tunable spectrum of ground and excited state properties. Such great diversity derives from strong competition among the charge, spin, and lattice degrees of freedom. They also figure prominently in a broad class of technological applications, stemming primarily from their favorable processing, fabrication and performance properties.

Electronic and Optical Process in Novel Semiconductors for Energy Applications

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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$499,000

Advanced energy technologies require high-performance materials, which in photovoltaics translates to new semiconductor materials to efficiently absorb sunlight, and in solid-state lighting (SSL), to new semiconductor materials for direct conversion of electricity to white light. A goal of this project is the realization of semiconductor materials 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 green emitters for SSL, via technologies based on GaAs substrates. A key to transcending the present limitations, is the understanding and control of fundamental electronic and optical processes in semiconductors, which is another goal of this project. Towards this, this project will focus on understanding the phenomena of spontaneous ordering in high bandgap lattice-mismatched GaxIn1-xP, and abnormal electronic structure and properties of isoelectronic dopants 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 semiconductor material with novel, useful properties.

Atomistic and Mesoscopic Study of Metallic Glasses

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Funding: $1,005,000

The goal of this project is to develop fundamental understanding of the structure, dynamics and deformation mechanisms of metallic glasses over multiple length scales, from the atomistic to the mesoscopic. At the atomistic level, analytical theory, molecular dynamics simulations, and first-principle calculations are used to investigate the atomic dynamics in the liquid state, the glass transition, mechanical deformation, and glass formability. We focus on the dynamic fluctuation in the local topology of the atom connectivity network, represented by the novel concept of atomic-level stresses and their dynamics. The mechanism of mechanical deformation is studied through the molecular dynamics simulation of steady state flow, including those under extreme conditions of very high stress and high temperature. Experimentally local atomic dynamics in the liquid is studied by neutron inelastic scattering, while local atomic rearrangements in the glass that occur during deformation and annealing are probed using synchrotron x-ray and pulsed neutron scattering. At the mesoscopic level, strain localization is investigated to determine the mechanism of mechanical deformation. Constrained plastic deformations are investigated across multiple length scales with a view to understand how to prevent catastrophic shear localization. The ultimate goal is to develop broad scientific principles for the alloy design of new materials for energy applications in a prescriptive manner.

Early Career: Spatially Resolved Ionic Diffusion and Electrochemical Reactions in Solids: A Biased View at Lithium Ion Batteries

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Funding: $500,000

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.

Exceeding the Planck Free-Space Energy Transfer Limit through

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Funding:	$600,000

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 thermo-photovoltaic approaches are not effective. There are two components to our approach. The first component is maximizing the near-field spectral energy density through the utilization of photonic surface states of nanostructures or planar materials. This requires 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 allow for the extraction of the enhanced near-field energy at rates that exceed the Planck free-space limit.

RECENT ACCOMPLISHMENTS

Emission enhancement and spectral tailoring of broadband emission of PbS quantum dots have been demonstrated using the enhanced photonic density of states of photonic crystal microcavities and waveguides. This program seeks to realize the same type of spectral control using thermal sources. Ultimately, we want to realize a near-field energy transfer rate beyond the free-space limit. Any material or structure used for this application must be stable at high operating temperatures (beyond what quantum dot emitters can endure). One system we have explored is the surface plasmon polariton state of indium tin oxide (ITO). This conducting oxide naturally has the surface plasmon frequency in the infrared region and can potentially endure high temperatures. At elevated temperatures, thermal excitation of surface plasmons is expected to yield enhanced near-field thermal energy. We have performed careful measurements of the optical properties and surface plasmon dispersion relation for ITO. Using measured optical properties, we calculate the thermal spectral energy density using fluctuational electrodynamics. This computational capability allows us to evaluate a wide variety of plasmonic structures for spectral tailoring. Near-field energy transfer is an equally important aspect of this program. We have developed an efficient computational method to calculate thermal conductance for the sphere-plane geometry. This classic geometry enables careful comparison with experimental results. In addition, we have begun construction of two near-field probes that will allow us to out-couple the near field energy for spectral analysis.

PLANNED WORK

For the coming year our experimental efforts will focus on: (1) measurements of near-field energy transfer using sphere-plane geometry between heated ITO (or spoof plasmon surface) and a microsphere; (2) measurement of energy transfer dynamics using short laser pulses; (3) measurement of near-field spectral content using a waveguide probe on ITO (or spoof plasmon surface). Our theoretical efforts for the coming year include: (1) design of nanostructured surfaces exhibiting enhanced near-field thermal energy content; (2) design of a near-field absorber that can efficiently extract the enhanced near-field energy of the heated source; (3) development of a theory describing the dynamical aspects of near field energy transfer.

Field-Structured Composites

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Funding:	$459,000

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 has two thrusts: (1) the development of field-structured composite materials and (2) the stimulation of functional fluid flows.

The composites thrust focuses on 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 both advection lattices and chaotic advection in fluid suspensions. The advection lattices are a new and surprising discovery that appear 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.

RECENT ACCOMPLISHMENTS

This year's program has had scientific and technological impact on a number of areas. We have explored the use of both single-layer and multilayer magnetic platelets as the particle phase for thermally conducting field-structured composites. These composites have extremely large specific thermal conductivities, with enhancements as large as 23 with only 16 volume % particles. We have used these materials to quantify the effect of Kapitza resistance in limiting thermal transport, by comparing the thermal conductivity enhancement to the dielectric enhancement. We find the Kapitza resistance can reduce the specific thermal conductivity enhancement by as much as a factor of five. Simulations of heat transfer in multilayered platelets led to some surprising conclusions about the roles of thermal contrast and particle geometry in heat transfer. We have expanded our research on what we call Isothermal Magnetic Advection to triaxial magnetic fields and have discovered both new flow lattices, significantly more effective magnetic fields for heat transfer, and an intrinsically stochastic method of creating artificial "fingerprints" that have implications for authentication and treaty verification. The latter is a complex process wherein a triaxial field is used to generate uniform flow, then selected field components are turned off to produce a frozen pattern that is similar to a fingerprint. Each pattern has many defects, so this process can generate an essentially limitless number of differentiable tags. We have also built a system to quantify heat transfer in IMA and have shown it to be highly effective. Finally, a general theoretical analysis of the time-averaged interactions between anisometric particles in multiaxial fields has been completed. The case of rods has been worked out in detail and shows that an interaction symmetry completely unknown in nature can be created, leading to unique rod orientations in assemblies of nanorods. This is a significant advance for the science of self-assembly.

FUTURE WORK

Work for next year will focus on measurements of heat transfer in IMA; the stimulation of IMA with triaxial ac magnetic fields (at this time one field component is dc); the simultaneous measurement of the magnetic permeability and thermal conductivity of field-structured composites containing anisometric particles; and the numerical determination of the magnetic ground state of nanorod assemblies subjected to multiaxial magnetic fields. In the latter investigation we expect to observe entirely new dipole orientations in nanorod lattices, and these could lead to metamaterials having remarkable permeabilities.

Nanometer-scale Surface and Interface Phenomena

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Funding: $2,531,000

Our goal 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 spectroscopic electrochemical STM to probe changes in electronic properties in electrochemical environments.

SELECTED RECENT ACCOMPLISHMENTS

- We deciphered the low-temperature equilibrium arrangement of H_2O in the wetting layer on Pt(111) by interpreting STM images and DFT calculations.
- We discovered that graphene multilayers grow on Ru(0001) by a unique mechanism – new layers nucleate and expand underneath existing layers.
- We identified a complex relationship between where SiC grows and where graphene forms during graphitization on SiC in atmospheric pressures of Ar.
- We determined the factors that control graphene orientation on Cu surfaces.
- ToF-SIMS imaging of model Al-Cu alloys showed that in the absence of localized corrosion, pure Al oxide exists above both intermetallic Al_2Cu particles and the surrounding matrix, thus advancing our understanding of pit initiation.
- We developed procedures to produce ordered arrays of stripes (alternating “up-down” bands of atoms) on Si(001) and determined the mechanisms by which the stripes order.

PLANNED WORK

- Conduct fundamental investigations of dynamical processes on energy-relevant oxide surfaces.
- Investigate Li intercalation into layered materials.
- Determine atomic-scale mechanisms that control the growth and properties of graphene.

- Understand interactions between graphene and foreign atoms and deposited films.
- Investigate pattern formation in the wetting layer of doped ice.
- Investigate dewetting of metal films on solid-state electrolytes.
- Develop theory of the molecular arrangement, epitaxy and transport of water at wetting surfaces.
- Define the physical and chemical scale of pit nucleation and propagation structures for aluminum.
- Determine mechanisms governing cathodic kinetics across the passive layer on Al-Cu alloys.
- Tailor oxide surface stability for electrical energy storage.
- Investigate charge transfer through solid electrolytes using LEEM-PEEM.
- Develop new instrumentation such as Q-force AFM and spectroscopic LEEM-PEEM.

Novel Electronic Materials

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Funding:	$385,000

This project has two global objectives: first, achieve fundamental understanding of the mechanisms whereby atomic-, nano-, and micro-structure influence the electronic, optoelectronic, and mechanical properties of novel and advanced electronic materials; and second, by using such understanding, develop methods of nanoscale manipulation in growth and processing for the enhancement of technologically important macroscopic properties. The project is divided into two Subtasks described as follows.

Subtask 1, “Luminescence, Structure, and Growth of Wide-Bandgap Semiconductors,” is developing fundamental understanding of the optoelectronic properties of GaN alloyed with InN. The emission of bandgap light from InGaN is exceptionally strong and consequently of great technological interest for such applications as solid-state lighting (SSL). However, the light emission varies by orders of magnitude within content for reasons that are not yet fully understood. This project seeks to elucidate carrier transport and the interplay of radiative and non-radiative pathways for electron-hole recombination. To do so, we are combining optical and electrical measurements with materials characterization by x-ray diffraction, atomic force microscopy, and transmission electron microscopy, using specially grown microstructures and device configurations. Of particular interest are the influences of point and extended defects, compositional modulation, and heterointerface structure. Under Subtask 1, FY 2011 accomplishments include completion of work to develop an x-ray scattering model that simulates the combined effects of lateral film-thickness variations and interface grading on the diffraction of InGaN MQW superlattice heterostructures. By using the developed model to simulate measured (0002) diffraction patterns, we nondestructively reveal compositionally graded heterointerface widths in the range 0.5-1.1 nm coexisting with MQW film thickness variations of 1.1-4.2% rms in typical InGaN MQW heterostructures used for SSL and photovoltaics. Results of these diffraction-modeling studies are reported in a comprehensive manuscript recently submitted to the *Journal of Applied Physics*. Further accomplishments in FY 2011 include successful installation and testing of an ultra-fast streak camera and spectrometer system that enables time-resolved photoluminescence studies of carrier recombination processes in InGaN heterostructures. Finally, additional Subtask 1 work used power spectral density analysis of atomic force microscopy images to examine the competing roles of two key epitaxial growth mechanisms, surface diffusion and evaporation/recondensation. This work focused on how these mechanisms impact InGaN/GaN growth morphology and thereby influence green-wavelength luminescence intensity in InGaN MQW heterostructures. A paper explaining this work is in progress.

Subtask 2, “Atomic Processes and Defects in Wide-Bandgap Semiconductors,” seeks to elucidate the fundamental properties and reactions of point defects, impurities, and dopants in GaN and its alloys with InN and AlN. To achieve this objective, electrical, optical, spectroscopic, and compositional analyses are carried out under a variety of experimental conditions, and the results are interpreted through modeling that utilizes atomic configurations and formation energies obtained from density functional theory (DFT). Under Subtask 2, FY 2011 accomplishments include completion of DFT calculations of the formation energies of neutral & charged Ga vacancies in GaN, which were calculated for thirteen different hexagonal and orthorhombic supercell geometries ranging from 72 to 1024 atoms in size. Examination of the detailed effect of supercell size on the convergence of the defect formation energy reveals that calculated defect-formation energies of reasonable accuracy (converged to < 50 meV after application of Makov-Payne supercell-size corrections) require supercell sizes of at least 300-500 atoms for highly charged defects (defect charge $q=-2,-3$). Previous DFT studies of charged III-nitride defects have often used small supercells (usually < 200 atoms) and have tended to omit supercell size corrections, which may limit the accuracy achieved in many existing studies. A manuscript detailing the results of the DFT study is in progress. Subtask 2 experimental accomplishments in FY 2011 include deep level optical spectroscopy studies of dilute InGaN heterostructures (~ 2% indium mole fraction), which were undertaken to understand the impact of indium alloying on defect incorporation. The results indicated that defect levels near the valence band shift in energy with the band gap, while the energy levels of defect states closer to the middle of the band gap are not strongly impacted.

Elucidation of Hydrogen Interaction Mechanisms with Metal-Doped Carbon Nanostructures

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Funding:	$430,000

The purpose of this project is to understand how hydrogen interacts with pure and metal intercalated carbon nanostructures. By controlling the temperature and pressure at which hydrogen interacts with these materials, we are able to control the amount of hydrogen stored in the material which allows us to fine-tune the material’s properties based on the quantity of hydrogen present. While our initial interest in these materials was for hydrogen storage, we have recently determined that these materials have many of the desired properties for other energy storage/conversion devices (i.e., batteries, superconductors, etc.)

FY2011 HIGHLIGHTS

Publication: “Catalytic Effect of Fullerene and Formation of Nanocomposites with Complex Hydrides: NaAlH4 and LiAlH4.” Journal of Alloys and Compounds, 2011, 509S, S562– S566.

Invited Review Article: “Catalytic Carbon Nanostructures and Novel Nanocomposites for Hydrogen Storage” Journal of the South Carolina Academy of Science, 2011, 9, 13-19.

Accepted Manuscript: “Synthesis and Characterization of a Lithium Intercalated Fullerene Hydride for Reversible Hydrogen Storage” Nano Letters, 2011.

Research: We have been able to directly image our novel materials with nanoscale resolution before and after hydrogen desorption by SPM (Scanning Probe Microscopy) in order to determine any morphological changes that occur at the nanoscale during this process. We have also submitted a proposal to use the UHV-SPM at the BES Center for Nanoscale Materials at Argonne National Laboratory in order to obtain higher resolution images.

Research: We are also examining the effect that the presence or absence of hydrogen has on the bulk electronic and ionic mobility in our materials. By controlling the amount of hydrogen present in the material, the mobility of electrons or ions can be fine-tuned.

Synthesis and Processing

Institutions Receiving Grants

Plasmonic Nanostructures Integrated with Semiconductor Light Emitting Materials for Enhanced Efficiency and Functionality

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Funding:	$155,000

The general goal of this research 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 metal electron gas) 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 LEDs for 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. In addition, this project is aimed at the demonstration of a higher level of integration where metallic NPs are introduced inside (as opposed to on top of) the epitaxial material.

Large enhancements in photoluminescence efficiency have been obtained with this approach, as well as substantial collimation of the output light beam. From a basic science standpoint, these research activities also provide key information about the optical properties of metallic nanostructures, particularly those related to their ability to control fluorescence processes in their near field. Specifically, we have investigated a wide range of plasmonic excitations, 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. The demonstration of fluorescence control based on these excitations is directly related to their local field enhancements, resonance wavelengths and/or dispersion curves, and scattering efficiency, and therefore, allows gaining fundamental insight into these basic properties.

Mechanisms of Sputter Ripple Formation: Coupling Among Energetic Ions, Surface Kinetics, Stress and Composition

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Funding:	$125,000

Low energy ion bombardment induces a wide variety of morphological evolution, including the spontaneous formation of periodic structures (sputter ripples and/or quantum dots). Understanding the complex interactions controlling ripple formation provides unique insight into the processes controlling the evolution of surfaces and nanostructures and occurring in high flux environments such as nuclear reactors. Moreover, sputtering is an important process for surface modification (e.g., sputter depth profiling) and holds promise as an inexpensive method for forming nanostructured materials over large areas.

The objective of our work is applying targeted experiments and multiscale modeling to develop a deeper understanding of the fundamental mechanisms controlling ion-induced surface evolution. Systematic, quantitative experiments measuring ripple formation under a variety of processing conditions have been used to develop a kinetic phase diagram of the pattern formation behavior. Continuum models based on an instability mechanism demonstrate that the measured evolution can be explained within this simple paradigm. Kinetic Monte Carlo simulations prove that the atomistic mechanisms included in the continuum model lead to the type of patterning behavior predicted. Continuum and numerical models also predict the complex relaxation of surfaces that include the effects of atomic steps.

Recent work has focused on understanding the quantitative discrepancy between the measured ripple growth rate and the value predicted by the continuum theory. This difference suggested that there are other roughening mechanisms (such as stress) that enhance the ripple formation rate. We have therefore made measurements and calculations of the stress induced by low energy ion bombardment. A defect-based model, including implanted ions, vacancies, and interstitials, is able to explain the observations on crystalline Cu surfaces. MD calculations of the ion-surface interaction provide information about how the ion displaces atoms and generates stress in the layer. These calculations suggest that a novel dislocation-based relaxation mechanism is also possible to relax ion-induced stress. New results of sputtering of Si need to include the mechanism of viscous flow. We are currently using our results of stress evolution with different fluxes to develop a model for ion-enhanced viscous flow in Si at low energies.

Sputtering of alloy surfaces is being explored to search for a new form of composition modulation predicted by our models. We have also extended our modeling work to study alloy structures such as core-shell particles, heteroepitaxial multilayer's, nanowires, and surface ripples. For alloy systems, the growth law for a fully faceted structure requires the specification of the normal velocity of each facet, the incorporation rate of each alloy component on the surface, and the exchange of surface atoms with the bulk. By using only fundamental concepts of thermodynamics, we derived the governing equations for the growth of strained and fully faceted two-component crystals in regimes where surface material transport may be governed by surface attachment limited kinetics or surface diffusion limited kinetics.

Thermochemistry of Anion Defect and Charge Coupled Substitutions in Fluorite and Perovskite-Based Materials

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Funding:	$200,000

This proposal is for the renewal of grant DE-FG02-03ER46053, “Thermochemistry of Anion Defect and Charge Coupled Substitutions in Fluorite and Perovskite-Based Materials,” at the University of California at Davis, Alexandra Navrotsky, PI. The project emphasizes the thermodynamics of ionic substitutions and order-disorder in materials with high ionic conductivity. Such materials find important applications in solid oxide fuel cells, gas separation membranes, catalysts, nuclear fuels, and nuclear waste ceramics. Thus they are directly relevant to one of DOE’s basic missions, namely the development of more efficient energy sources and energy utilization. Fundamental and systematic thermodynamic data are essential for predicting possible new materials, for determining materials compatibility and longevity in use, for developing efficient synthesis and processing, and for assessing environmental impacts. From the point of view of basic science, this work addresses a number of DOE Grand Challanges as well as use-inspired fundamental questions. Understanding the relations of thermodynamics, structure and bonding addresses the Grand Challange of “how do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?” The materials studied address basic research needs for the hydrogen economy (solid oxide fuel cells, separation membranes, catalysts) and for advanced nuclear energy systems (reactor fuels and waste forms).

The new project expands the range of materials studied to include some exciting new ceramics, different defect mechanisms leading to ionic conductivity, and mixed ionic/electronic conductors. It puts greater emphasis on the energetics of interactions at surfaces and interfaces. Specifically, work on fluorite-based solid electrolyte oxides will include further exploration of the recently discovered strong linkage of the thermodynamics of mixing and the ionic conductivity maximum; as well as the calorimetric study of nanopowder and dense nanocermaic yttria stabilized zirconia to obtain surface and interfacial energies. The thermodynamics of apatite and melilte materials, two new groups of interstitial oxide ion conductors, will be investigated. Thin film and bulk transition metal perovskite solid solutions will be studied. High temperature oxide melt solution calorimetry is the principal and unique technique utilized. In addition, thermal analysis, heat capacity measurements, and X-ray diffraction, infrared spectroscopy, and other analytical tools will be used. A new apparatus with capabilities for synthesis of anhydrous nanopowders by condensation from vapor, high temperature levitation and quenching of disordered and amorphous ceramics, and thermal analysis at high temperature (1500-3000 °C) using optical spectropyrometry will be constructed.

Metal Oxide Core Shell Nanostructures as Building Blocks for Efficient Light Emission

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Funding:	$176,000

The development of materials for more efficient generation, storage, and conversion of energy is one viable approach to reduce energy consumption in lighting, which accounts for about 20% of the global consumption of electricity. Amongst all materials, rare-earth-ion based phosphors are particularly important because of their versatile applications in fluorescent lamps, light emitting diodes (LED), fiber-optic amplifiers, lasers, bioimaging, electroluminescent displays and solar cells. Phosphors with reduced dimension and dimensionality are of great interests because the resulting optical performance can be engineered by manipulating the effective index of refraction and dopant concentration and spatial distribution.

The goal of this research is to synthesize core-shell nano-structured metal oxide materials and investigate their structural, electronic and optical properties to understand the microscopic pathways governing the energy conversion process, thereby controlling and improving its efficiency. To rationally design such a core-shell nano-structured metal oxide material with larger absorption cross-sections, this work will tackle two critical aspects of the materials engineering: (1) elucidate the growth mechanism of these nanostructured materials and its effect on the resulting photo-efficiency and (2) control the spatial distribution of optically active rareearth ions by atomic layer deposition; as the location and spatial distribution of the rare-earthions as well as the microstructure and morphology are critical to the optical performance of these materials at reduced dimension and dimensionality. Specifically, this program will focus on: a) developing a hydrothermal process to synthesize the nanometered core and a radical enhanced atomic layer deposition process to control the distribution and activity of the dopant ions in the shell, b) monitoring the formation of metal hydroxides and metal oxide nanostructures by synchrotron radiation based x-ray absorption and diffraction analyses, c) identifying the chemical coordination of the rare-earth ions in the host and quantifying the concentration of optically active rare-earth ions, d) measuring the photoluminescence of these nanostructures (individually and as an ensemble) and determining the absorption cross section for rare-earth ions and its dependencies on the doping concentration and the host composition, and e) integrating these synthesized one-dimensional rare-earth doped materials into simple devices to test their optical performance. The success of this research will provide optimized processes for synthesizing complex rare-earth ion doped metal oxide nanostructures and thin films, and lay the foundation of future generations of optical devices with higher energy efficiency.

Atomic Layer Deposition (ALD) of Metal and Metal Oxide Films: A Surface Science Study

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Funding: $186,000

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 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 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 (XPS), Auger electron (AES), low-energy ion scattering (LEIS), temperature programmed desorption (TPD), and infrared (IR) 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.

Synthesis & Engineering of Submonolayer Type-II Quantum Dots to Enhance Material Properties of Wide Bandgap Semiconductors

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Funding: $200,000

Semiconductor heterostructres 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. Type-II ZnTe/ZnSe quantum dots (QDs) are particularly interesting because of their relatively large valence band and conduction band offsets. Furthermore, II-VI wide band gap semiconductors, such as ZnSe, have long been difficult to dope p-type. This difficulty still constitutes a problem for practical uses of these materials, non-withstanding the promise of such a material in light emitters in the blue-green spectral region. Previously, a high net acceptor concentration of 6×10(18) 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, and Hall effect measurements of hole concentration and mobility could not be made. It was concluded that although high net acceptor concentrations were achieved, 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, a series of samples were grown with Mg added to the ZnTe QDs. Initial characterization, carried out during our first year funding period, showed that the Mg was contained primarily within the QDs (they exhibited typical type-II QD behavior) and that, for the first time, we were able to measure free hole concentrations using Hall effect. This was interpreted as a demonstration of our hypothesis that the band offset of the new ZnMgTe QDs; as a result, the hole confinement had been reduced in these samples. 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 confirmed our earlier reports that our ZnTe/ZnSe samples exhibit magneto-PL behavior that can only be explained by the formation of QD. Magneto Pl measurements also provided 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 photovoltaics.

Asymmetric Hybrid Nanoparticles (AHNs)

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The project is concerned with the development and synthesis of nanostructures of complex compositions. One example is hybrid nanoparticles that are composed of a metallic core with caps of different materials deposited on the core surface. The hybrid nanoparticles have the potential to exhibit properties that can be tailored by selecting different combinations of the core and cap materials as well as by changing their dimensions. The emphasis is on plasmonic hybrid nanoparticles that have a silver core. Silver nanostructures exhibit the most efficient interaction with visible light compared to all other materials due to the excitation of plasmon resonances. Such efficiency makes plasmonic hybrid nanoparticles attractive for various applications that involve the interaction with light including light harvesting for photovoltaic devices. The current focus is on the synthesis of two stacked caps made of p- and n-doped semiconductors on the surface of the silver plasmonic nanoparticles. The two caps comprise a rectifying pn-junction that is known to produce photovoltaic effect. The material of choice for the semiconductor caps is cuprous oxide. Cuprous oxide is a non-toxic, abundant material that can be made to exhibit p- and n-type conductivity, thereby providing a possibility for pn- homojunction.

While cuprous oxide photovoltaic devices were previously fabricated, they exhibit low, under 2%, overall efficiency. We hope to significantly improve the efficiency by employing plasmonic silver nanoparticles as light capturing antennae. By shifting the role of light capturing away from the pn-junction we can reduce the thickness of the pn-junction thereby improving its conductivity. Low conductivity of the junction, particularly n-type cuprous oxide, was one of the main factors limiting the efficiency of the previous devices; and n- and p-type cuprous oxide is electrochemically deposited onto silver nanoparticles assembled into two-dimensional arrays on conducting substrates. Space between the particles in the array is filled with an insulating polymer by spin-coating, so that the deposition takes place on the surface of the particles and not on the conducting substrate. The advantage of the electrochemical deposition method stems from its versatility, low cost, and amenability for large scale processing. By changing electrochemical conditions, n- and p-type cuprous oxide can be sequentially deposited resulting in a pn-homojunction. We have already demonstrated n- and p-type photoconductivity from the corresponding cuprous oxide caps on silver plasmonic nanoparticles. The next target is hybrid plasmonic nanoparticles with the pn-homojunction.

Molecular Hydrogen Storage in Novel Clathrate Materials

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The present award has three key objectives that are vital towards realizing the potential of this new class of energy storage materials: (1) self-preservation metastability – hydrates preserved outside equilibrium conditions, (2) structure/phase metastability – coexistence/transitions of metastable phases, and (3) metastable cage composition/occupancy – variable cage occupancy and dynamics.

The questions on metastability are pivotal in all energy applications of clathrate hydrates, including energy storage, energy transportation, and energy recovery. Our most recent advancements are providing new insight into synthesis and structure (objective 2) and cage dynamics (objective 3). Specifically:

- The formation mechanisms and elementary building blocks of clathrate hydrates have been identified, showing seven common cages in hydrate nucleation.
- Microsecond-scale simulations of clathrate hydrate nucleation and growth have been performed.
- H_2 storage capacity (3.4 wt. %) has been increased with a breakthrough synthesis method of solid-solid mixing. The effectiveness of the synthesis method was shown to be largely dependent on pressure.
- Rapid growth of H_2 hydrate has been observed in the presence of preformed hydrate templates.
- The rapid templating behavior of clathrates is being utilized as a possible mechanism for the formation of metastable H_2 hydrate structures other than sII, which could have implications for higher storage capacity of H_2 and other guests in clathrates.

This current research builds upon our knowledge of the fundamental science of key processes controlling the synthesis and structures of clathrate hydrates containing H_2 and other guest molecules for energy storage.

Achieving Three-Dimensional Well-Ordered Nanostructures in Block Copolymer Films by Combined External Fields

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Block copolymers have great potential for applications in nanotechnology, due to their self-assembly into spatially periodic structures on the length scale of 10 to 100 nanometers, direct control of the size and shape of these nanostructures (morphology), and the uniformity of these nanostructures. Many applications (e.g., templates for nanolithography, nanowires, high-density storage devices, and nanostructured membranes) envisage thin films of block copolymers supported on a substrate, and well-ordered nanostructures oriented perpendicular to the substrate are desirable. Unfortunately, due to defect formation and slow kinetics common in block copolymer systems, the order of the self-assembled nanostructures persists over only a few hundreds of nanometers. Control of both the perpendicular orientation and in-plane ordering of the morphology to achieve long-range (over microns) order are therefore the key issues in many applications. External fields, e.g., shear, electric fields, topographically or chemically patterned substrates, have been successfully applied to control the orientation and ordering of self-assembled morphologies of block copolymers. But none of these can be used alone to achieve nanostructures with long-range three-dimensional order that are defect-free.

We propose a three-year, computational study on the simultaneous application of two orthogonal external fields to obtain such well-ordered structures. In particular, for the self-assembled lamellar or cylindrical morphology in diblock copolymer films, we will use a topographically or chemically patterned substrate to control in-plane ordering, and an electric field applied perpendicular to the film to achieve the desired perpendicular orientation. Using 3D self-consistent field calculations combined with finite element methods, we will investigate the impact of key controlling parameters, including substrate pattern (size, symmetry, period, and interactions with the two blocks), electric-field strength, and film thickness. The finite element methods offer great flexibility in handling the boundary conditions in the self-consistent field calculations (e.g., on topographically patterned substrates). Our overall goal is to identify the optimal conditions under which perpendicular nanostructures (lamellae and cylinders) with long-range 3D order can be obtained by combined external fields, which will allow knowledge-based rational design (instead of trial-and-error experiments in a large parameter space) to achieve such nanostructures. This knowledge is of paramount interest to many applications of block copolymers in nanotechnology, including nanolithography, high-density storage devices, quantum dot or anti-dot arrays.

In addition to the above outcome, this work will also greatly further the understanding of the use of topographically patterned substrates to induce long-range order of self-assembled block copolymers. Such knowledge is very useful in guiding the experimental design of graphoepitaxy to achieve desired morphologies for targeted applications. Moreover, through quantitative comparison of different aligning mechanisms proposed, this work will reveal their relative contributions to the electric-field alignment of block copolymer microdomains, which is of both fundamental and practical importance. Our study on the competition between the surface preference and the electric field applied perpendicular to the film will provide us with a more complete understanding of the phase behavior of block copolymer films under electric fields. Finally, although we focus on diblock copolymers here, our approach applies equally to block copolymers of other molecular architectures, e.g., triblock or multiblock copolymers, and their blends with homopolymers or other block copolymers, which offer almost unlimited possibilities for the morphological control in various applications. Our original approach of combining self-consistent field calculations with the finite element method as proposed here can also be readily extended to other polymeric systems having complicated boundary conditions or sharp variations, such as the free surface between block copolymers and air/vacuum, polymers on curved surfaces, polymer nanocomposites, etc. Given the great success of self-consistent field theory in describing the equilibrium behavior of polymeric systems, this work will generate a powerful computational tool for studying soft materials.

Control of New Kinetic Barriers & Design of Nanorods

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Nanorods are enabling blocks of energy technologies. While synthesis of nanorods has been a common practice, it is critical to understand the fundamental principles that govern the synthesis. Using a combination of atomistic simulations, analytical formulation, and physical vapor deposition experiments, this team aims to identify characteristic length scales of growing nanorods and establish connections between these scales (in the period of 2011-2014). Further, based on the scientific understanding the team will add to the science-based synthesis of nanorods. The results will impact the advancement of surface science, particularly its form at the nanoscale; and the advancement further forms the basis of synthesis for sustainable energy technologies.

Self-Assembly of Non-Spherical Colloids:New Reduced Symmetry Crystals and Nesophases for Templating Functional Materials at Fine Scales

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Mesoscale control of light-matter interactions as a route to enhance performance in a range of technologies is a central aim in colloidal materials science and engineering. Increasing focus on atypical colloidal structures is uncovering novel partial order mesophases, quasicrystals, and superlattices with dramatic effects on photon dispersion relations. This work explores processing-microstructure relationships for the self-organization of nonspherical colloids under confinement and exposed to shearing conditions. How nonspherical particle mesophases adapt in the presence of surfaces and how shear forces drive development of structure and rheological behavior in these systems will be investigated. Wedge cell and parallel plate confinement techniques and shear-assisted assembly will provide a platform to understand the role of thermodynamic and non-equilibrium effects including dynamic flow behavior on the formation of complex colloidal structures. Inorganic precipitation and seeded emulsion polymerization will be employed to synthesize tailored collapsed particle morphologies from hemispheres to bulbous mushroom caps as well as faceted polyhedra and peanut shapes. Real space quantitative analysis of structural evolution as a function of shape parameters, volume fraction and confinement heights, specifically in the thin film regime from five to ten particle monolayers, will be conducted using ultra-fast confocal microscopy to track particle motions. Confinement induced phase transition mechanisms such as vicinal surface rearrangement will be probed. A custom confocal rheometer setup will be utilized to map structural and rheological behavior as a function of confinement gap size and shear rate at a variety of volume fractions. Computational studies on phase behavior of anisotropic particles, kinetics and mechanisms of ordering transitions, and rheology of ordered phases will be conducted to complement experiments. For this purpose, advanced molecular simulation methods will be used including, forward flux sampling (to probe the kinetics of phase transitions) and non-equilibrium iso-stress molecular dynamics (to detect yield stress behavior). Ultimately, a range of materials with complex architectures and symmetries will be obtained by infiltrating the assembled templates with semiconductors and high refractive index ceramics using nanoparticle co-assembly, sol precursor co-assembly, and vapor (atomic) layer deposition.

Using Interfaces To Create Strongly-Coupled Magnetic-Ferroelectrics

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The proposal involves two goals that have never yet been achieved in multiferroics that are a) to create a ferromagnetic ferroelectric that can be switched between symmetry equivalent states with an electric field and b) to create a magnetic ferroelectric where magnetism can be switched on by applying an electric field. Multiferroic materials that operate at room temperature would be also highly desirable. The technical result will be the electrical control of magnetism, envisioning magneto-electronic devices with huge magnetoelectric coefficients. This could result in new magnetic random access memory devices or spintronic devices. In addition, if huge magnetoelectric coefficients are achieved, the magnetization will be able to be tuned and therefore, tunable microwave filters, delay lines, phase shifter, and resonators as well as magnetic field sensors, and actuators can be imagined. Moreover, along the way in designing these new materials the proposed method will also provide a way for rationally designing oxide heterostructure materials. The approach involves first principle theory coupled with crystal chemistry and symmetry analysis to design and identify a real material that will not necessarily be prepared by conventional bulk synthesis methods and also may not exist in nature. The materials will be designed from the bottom up with careful attention to the interfaces. MBE will be used to grow the materials. Scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS) and in situ x-ray scattering will be used to characterize films on the atomic level. The magnetic and magnetotransport properties and x-ray magnetic dichroism (XMCD) of these heterostructures will also be measured.

Improved Electrochemical Performance of Strained Lattice Electrolytes via Modulated Dopling

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Funding: $137,000

Solid electrolytes, found in batteries, fuel cells, and chemical sensors, are highly (and increasingly) important energy technology components. Nevertheless, the rigid atomic framework of solids provides for relatively few materials with high ionic conductivity, particularly at low temperatures. For example, solid oxide fuel cells typically must be operated at = 800 °C in order to obtain sufficient oxygen ion conduction through the electrolyte. These temperatures necessitate the use of expensive components and limit device lifetimes, making them economically unfeasible at this time. Recently, the use of nanostructured multilayers has been proposed as a means to obtain vastly improved solid state ionic conduction. Unfortunately, the experimental evidence advocating these techniques has often been controversial. In addition, nearly all of the multilayers demonstrated have used layer materials wherein one of the layers was a poor ion conductor. Here, we propose to sputter deposit nanostructured, pseudo-homoepitaxial multilayers of oxygen ion conductors. Ionic analogues of the high electron mobility transistor (HEMT) will be formed by modulation of the dopant and host atom concentrations, thereby forming high ionic mobility electrolyte layers in close proximity to layers with high dopant (and thus defect) concentration. Impedance spectroscopy will determine the effects of the spacing and magnitude of compositional modulation on both ionic conductivity and surface exchange. Oxygen ion conductors, with application to SOFCs, will be used in this study; however, the concepts and methods discovered will be applicable to other ionic conduction systems.

Nanoparticles Stabilize Thin Polymer Films: A Fundamental Study to Understand the Phenomenon

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The ability to control phase separation of polymer – nanoparticle blends in thin films is fundamental to the design of next generation interfaces and membranes. The objective of this study is to control the phase separation of nanoparticles to the film interface or within the film bulk to make unique materials and membranes at will.

This is accomplished through a fundamental understanding of the thermodynamic interactions between the components dictated by their nanoscale size and the fact that they are confined within a film. The factor that controls phase separation, or assembly, is entropy which is incredibly robust. A polymer chain loses many degrees of freedom next to a substrate since monomers pinned there influence those along the backbone and a large entropy reduction results. Yet, a particle will only lose three degrees of freedom at the same interface and so an overall system entropy gain results if the polymer pushes the nanoparticles to the substrate and sits on this nanorough carpet.

In fact, the nanoparticle assembly energy is so large that a polymer film will wet an energetically unfavorable surface since the energy cost is too great to disassemble the nanoparticle layer. In addition, the polymer film will not dewet from substrates having roughness greater than the film thickness so it is possible to have a rough liquid surface. Again, entropy controls this phenomenon. A curved liquid surface has an associated pressure rise which will tend to flatten the film; however, to flatten the film requires dewetting from the protrusions and disassembling the nanoparticle layer. The assembly energy to the substrate is so great that dewetting is avoided and a rough liquid surface results.

Presently, new membranes and films are being developed by controlling the above factors since addition of nanoparticles to thin polymer films promotes phase separation to the substrate and around larger objects placed within the film. Confirmation of the phase separation, or assembly, has been confirmed and the factors controlling the phenomena are being investigated. Generalization, design, and fundamental understanding of these processes are achieved through a long-standing collaboration with Dr. Amalie Frischknecht at Sandia National Laboratories, through the Center for Integrated Nanotechnology (CINT). Dr. Frischknecht's theoretical efforts encompass classical density functional theory (DFT) together with other continuum techniques to model and design unique materials.

The significance of this research is that nanoparticles packed around larger particles could make new, spherical band structures; or if enough nanoparticles are present, then percolative pathways may be promoted through the film as they phase separate. This could have application in polymer-based solar cells which require conductive pathways to extract electrons. Also, making various shaped, three-dimensional surfaces could be used to mediate cell behavior or develop lenses of nanoscopic dimension, among other uses.

Nanoscale Morphology Evolution under Ion Irradiation

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The use of ion beams has great promise for morphology control in materials synthesis and processing at sub-lithographic length scales. We are studying experimentally and theoretically 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. 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 fundamental understanding and combined with known templating methods, then useful periodic structures as small as 7 nm could be generated in high-throughput settings.

Synthesis of New Diamond-Like B-C Phases Under High Pressures and Temperatures

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Funding: $195,000

This year, we repeated the synthesis of the diamond-like BC_x phase under the high pressure and high temperature (HPHT) conditions we obtained last year and finished characterization of the new phase. Analysis of the atomic structure and elemental composition by high resolution electron energy loss spectroscopy (EELS) has confirmed that the synthesized phase is cubic BC_3. High resolution transmission electron microscopy images also confirm that the *c*-BC_3 sample is single nano-phase. The electron diffraction pattern of the nanocrystalline *c*-BC_3 sample shows the same zinc-blende structure revealed by synchrotron x-ray diffraction (XRD). The new phase can be indexed by a cubic unit cell with lattice parameter, $a_0 = 3.5866 \pm 0.0003$ Å.

This year, we found that a dense $BC_{1.8}$ layer could be deposited using low-pressure thermal chemical vapor deposition (CVD). The electrical properties of the $BC_{1.8}$ and $BC_{8.2}$ films were measured by a four-point probe system. Resistivity of several films appeared to be ($1.5\text{-}3.0\times10^{-7}\ \Omega$ m) as low as that of iron ($1.0\times10^{-7}\ \Omega$ m). The behaviour of resistance of $BC_{1.8\text{-}8.2}$ layers as a function of temperature is similar to that of semiconductors. This finding indicates that it is possible to obtain hard BC_x phases at nearly ambient conditions with conductivity similar or higher than that of graphite.

To understand the mechanism of the transformation of graphitic phases with sp^2 bonds to novel denser phases with sp^3 bonds and the HPHT conditions of such transitions, we carried out Brillouin light scattering (BLS) measurements from a graphitic C_3N_4 (*g*-C_3N_4). Graphite and graphitic BCx phases are non-transparent phases and therefore, cannot be studied in DAC under high pressure by BLS. The *g*-C_3N_4 phase becomes transparent under high pressure and BLS measurements provide unique opportunity to study elastic behavior of the graphitic ring under high pressure. Comparing the behavior of the Raman peaks line width of graphite under pressure and that of melamine leads us to conclude that C_3N_3, or the *s*-triazine ring, is more rigid than the C-C graphite ring.

Under the current DOE project, we successfully developed in a collaboration with our colleagues from the University du Monde, Le Mans, France, a new method for direct measurement of sound velocities (longitudinal and shear velocities) for opaque materials under high pressure in a DAC. It was demonstrated recently that, using laser ultrasonics (LU) in diamond anvil cells (LU-DAC), it is possible to detect and measure both longitudinal and shear velocities of a non-transparent iron layer in DAC at pressures up to 23 GPa. The main advantage of the LU-DAC point-source - point-receiver technique for non-transparent amorphous solids and melts is that it does not require any additional data (such as thickness of the specimen in DAC) for determining the elastic properties of the iron at high pressures. This year we installed the LU-DAC system in our laboratory.

Laser Fabrication of Active Single-Crystal Architecture in Glass

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There is a growing interest in the families of special glasses such as chalcogenides, which have low phonon energy and high polarizability that lead to high transmittance in the infrared region, higher refractive index, semiconductivity and an overall higher sensitivity to light. Several applications such as data storage and integrated optics depend on the ability to create and modify optically or electrically active elements on glass. In this respect, laser direct-write method has been successfully demonstrated for fabricating active ferroelectric single crystal architecture in a model oxide glass. This project attempts to extend the same basic concepts to chalcogenide glasses, which respond significantly differently to laser irradiation than oxides. Our current understanding of laser crystallization of oxide glasses suggests that photoinduced thermal effects are the primary driver of crystallization. However, preliminary results on chalcogenide glasses indicate contribution of other photostructural changes such as photo-expansion/contraction, photoplasticity, and field induced atomic movement in the transformation of glass into crystal, but essentially absent in oxide glasses and therefore appear to affect the crystallization of the former. A fundamental understanding of these photo-effects on crystallization is a special aspect of chalcogenide glasses, which is the focus of this study.

Two glass compositions in the Ge-Sb-S-I system 10GeS2.90SbSI and 20GeS2.80SbSI are selected for laser writing of SbSI single-crystal, a well-known chalcogenide ferroelectric and semiconductor for thermoelectrics. Initial observations demonstrate the formation of such single crystal line by Electron Backscattered Diffraction (EBSD), and Piezoresponse Force Microscopy (PFM) indicates its ferroelectric functionality. However, the profile of the structure is complex and crystallization process is sensitive to the position of laser focal point with respect to sample surface. Indeed surface quality of the samples has a large effect on the crystallization process as an uneven surface can change the focus depth of the laser light. We are evaluating the impact of this processing parameter on carefully prepared flat samples. In parallel, we are investigating photoinduced effects inasmuch as they determine morphology and orientation of laser formed crystals. Micro-Raman spectroscopy is being developed for the in situ monitoring of the crystallization stages using two independent lasers, one to probe the structure and another to cause photostructural changes. The use of separate probe and excitation laser would avoid fluorescence from the sample and allow changing laser parameters independently, which can be crucial for optimizing the Raman output and studying the effects of excitation laser parameter such as power, focal spot size etc. on crystallization. In due course, PFM will be used further for characterizing the orientation, crystallinity, ferroelectric response and domain structure of laser-written micro and nano structures.

Utilizing Molecular Self-Assembly to Tailor Electrical Properties of Si Nanomembranes

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The objective of this project is to use silicon (Si) nanomembrane, a well controlled two-dimensional single crystalline semiconductor, as a prototype system to explore the mechanistic basis of electronic interactions at the hetero-interface and to develop strategies to tailor nanomembrane’s transport properties by surface functionalization and self-assembly. Understanding and control of hetero-interfaces between organic and inorganic materials is crucially important for the development of organic electronics, molecular electronics, molecular/biological sensors, and energy converting devices. However, an atomic- and molecular- level understanding of charge transfer behaviors at the interface and how they influence the properties of inorganic materials remains elusive. This work will 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 may lead to the rational design of nanomaterials with controlled properties via regulation of surfaces and interfaces.

Brush-Coated Nanoparticle Polymer Thin Films

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Polymer nanocomposites (PNCs), the focus of this research program, are a technologically important class of materials that exhibit diverse functional properties, from optical and electronic to biomedical and structural. The properties of PNCs are determined not only by the chemical composition of the polymer host and the functionality of the nanoparticle, but also on the nanoparticle size, dispersion, organizational order in some cases, inter-nanoparticle separation distances, and on the relative interactions between the nanoparticles and the host. 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.

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 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. Specific systems include (1) brush-coated metallic nanoparticle/homopolymer, (2) brush-coated metallic nanoparticle/polymer-A/polymer-B mixtures, and (3) brush-coated metallic nanoparticle/diblock copolymer mixtures. Specific problems include, coarsening phenomena, dynamics of chains and of nanoparticles, surface mechanical properties, and surface plasmon absorption.

Understanding and Controlling Nanoscale Crystal Growth using Mechanical Forces

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Growth of one-dimensional nanostructures such as carbon nanotubes (CNTs) and silicon nanowires (SiNWs) 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. In this program, we will explore how mechanical stimulation may be used to control the formation rate, geometry, and perfection of one-dimensional nanostructures; and thereby aim to understand how mechanical stress affects the growth of crystals at the nanoscale. Specifically, we will study growth of CNTs and SiNWs because their basic growth processes are well-known, yet there is important need to more precisely control the structure and properties of CNTs and SiNWs for many applications. For this purpose, we are constructing micromanipulation systems for application of controlled forces to one-dimensional nanostructures during growth. 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. Since the program began in September 2010, we have focused on two main tasks: (1) design and fabrication of a new CVD growth chamber that will enable in situ manipulation of nanostructure growth and (2) analysis of the population dynamics of CNT ensembles (forests), enabled by high-resolution mapping using X-ray scattering.

Hydrodynamic Self-Assembly of Topographical Patterns on Soft Materials

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Funding:	$80,000

The surface topography of a material can have a significant impact on its optical, adhesive, and wetting properties. This grant supports our effort in using theoretical tools to explore novel ways of creating surface topography on soft materials that make use of principles from hydrodynamics and self-assembly. A particular area of emphasis is the self-assembly of sub-micron-scale patterns on the surface of polymer films subject to electric fields. Other areas of emphasis include topographical patterns created by evaporation of particle-laden liquid films and dewetting of liquid films on patterned surfaces. The methods being employed are theoretical in nature and include lubrication theory, linear stability analysis, and numerical simulation (finite-difference methods). Exploratory theoretical studies of the type proposed will help stimulate experimental work and guide that work to regions of parameter space where new phenomena are expected.

The merit of the proposed work lies in its exploration of fundamentally new ways of creating and controlling surface topography that make use of principles from hydrodynamics and self-assembly. These methods are worthy of exploration because they have the potential to considerably advance state-of-the-art technologies as well as fundamental scientific understanding. The proposed work is significant because it will develop novel concepts for controlling the surface topography of soft materials (e.g., polymer melts, polymer gels), a characteristic known to have a significant impact on optical, adhesive, and wetting properties in technological applications such as coatings, biomaterials, and microfluidics.

Epitaxial Electrodeposition of Metal Oxide Thin Films and Superlattices for Energy Conversion and Storage

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Funding:	$175,000

The focus of our research is the epitaxial electrodeposition of metal oxide films and superlattices from aqueous solution. The electrodeposited materials are semiconductors, magnetic materials, or electronic materials that can be used for energy conversion, storage, or to produce electronic devices which operate more efficiently. This year we continued our work on the electrodeposition of metal oxide films and superlattices based on magnetite and on the chemical bath deposition of ZnO nanospears. We demonstrated that epitaxial films of magnetite can be electrodeposited onto single crystal Ni(111), and that epitaxial films of CuI and CuI/Cu nanocomposites can be electrodeposited on the low-index faces of single-crystal Au. We continued our research on the electrochemical reduction of epitaxial metal oxide films to epitaxial metal films. Epitaxial films of magnetite were electrochemically reduced to epitaxial films of Fe in aqueous solution at room temperature. The orientation of the Fe was determined by the orientation of the substrate instead of the orientation of the magnetite, and the reduction began at the substrate/film interface instead of the film/solution interface. In addition to demonstrating that epitaxial magnetite can be reduced to epitaxial Fe, we showed in unpublished work that epitaxial bismuth oxide can be reduced to epitaxial Bi. Epitaxial Bi is of interest because of its very large magnetoresistance. A Grand Challange (i.e., very high risk but equally high payoff) in this work that would be very relevant to DOE would be to produce epitaxial Si films by the electrochemical reduction of amorphous silicon dioxide films. This would require nonaqueous solvents or molten salts, but it might prove to be an inexpensive method to produce large-scale Si films for photovoltaic applications.

Another new result this year was the demonstration that vanadium dioxide films can be electrodeposited by the electrochemical reduction of V(V) in aqueous solution, followed by a short anneal at 400 oC. The intensely blue material undergoes a metal-insulator phase transition at about 68 oC, so it is of interest for room temperature solid-state memory, high-speed switches, memristors, MottFETs, and electrochromic applications.

New Pathways and Metrics for Enhanced, Reversible Hydrogen Storage in Boron-Doped Carbon Nanospaces

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Funding:	\$320,000

Recently, carbon-based materials have shown a much richer spectrum of candidates for high-capacity reversible storage of molecular hydrogen by physisorption. Our research group has focused on the development of these materials by optimization of their geometries (surface areas, pore volumes) and enhancement of the adsorbate-adsorbent interaction energies by doping the carbon with boron at modest concentrations. Many of the relevant results are from our own work, mostly from previous grant periods (e.g., record-breaking storage capacities for H_2 adsorption in very high surface area activated carbons; the *ab initio* computational validation that boron doping of carbon may raise the H_2 binding energy to 10-14 kJ/mol, significantly raising the room-temperature storage capacity—later verified experimentally; and successful synthesis of carbons with a large volume fraction of mono-disperse sub-nm pores). In what follows we report on *some* of the most significant progress during the reporting period.

(a) Design and construction of sub-critical H_2 instrument (20 K). We have recently completed the construction of a Sievert sorption instrument to be used for sub-critical H_2 adsorption (awaiting the arrival of an ordered closed-cycle refrigerator). The new apparatus will permit determination of BET surface areas, and pore and skeletal volumes using H_2 rather than N_2, thus eliminating one possible source of error: the different pore structures probed by the different-sized molecules. The apparatus is expected to be able to operate with samples in the 0.05—5 g range, $0 < P < 200$ bar, $10\text{ K} < T < 800$ K (with $\Delta T = 10$ mK). This shows significant promise for new, more accurate, metrics of H_2 adsorption.

(b) Measurement of adsorbed film characteristics. Adsorbed film parameters (saturation density, thickness, and volume), specific surface area, and binding energy were determined using the Ono-Kondo lattice gas model and were validated to within 5% using Langmuir's model. Most notable, the saturation film density indicates an adsorbed phase density comparable to and, in some cases, surpassing the liquid density of hydrogen at the normal boiling point, which is in agreement with our earlier GCMC simulations. This is an important way to enhance the characterization of the materials and adsorption processes.

(c) Incoherent inelastic neutron scattering (IINS). Based on our theory of IINS off H_2 adsorbed in nanoporous carbon we conducted experiments at ORNL over an unprecedented broad range of energy and momentum transfer. We developed a novel theoretical methodology that permitted the classification of the H_2 excitations into localized and mobile states. This classification provides a measure of the planarity of the adsorption surface on the nm scale, and gives insight on the quantum states of adsorbed H_2 (previously we reported on the distinct nature of the adsorption isotherms for mobile and localized adsorption models). This will prove useful for our understanding of adsorption at the nanoscale.

(d) Adsorption mechanism and chemical bond studies using microscopic FTIR spectroscopy. Using a spot resolution down to 40 μm, reduces the "washing out" of the spectra due to local sample variations. This permitted us to, for the first time, directly observe the presence of B-C bonds in boron-doped carbon. We plan to use microscopic FTIR to study vibrational and rotational modes from hydrogen-hydrogen and other chemical bonds for hydrogen adsorption. This will help us to answer two basic questions: (1) what are the potential mechanisms of hydrogen adsorption in nanoporous carbon and (2) what are the properties of chemical bonds related to compositions and structures of carbon materials?

(e) Small-angle x-ray scattering (SAXS). Experiments were conducted at the Advanced Photon Source. We determined that typical polymer-based (usually PVDC) nanoporous carbons have pore structures that are significantly different than all activated bio-carbons, with the "SAXS knee" at a significantly lower Q. This feature correlates to the formation of a 34 Å pores with annealing of PVDC samples. In addition, we see the presence of a large number of 6-7 Å pores, vs. no pores under 10 Å for biocarbons.

(f) Boron doping via co-polymerization. B-functionalized carbons will be produced primarily through two techniques. The first is through cross-linking of poly(vinyl) alcohol with sodium tetraborate and various boronic acids. The polymer is initially cross-linked through hydrogen bonding. The sample is then heated and undergoes a dehydration reaction and boronic acid esterification. The sample is then heated further to produce boron-doped activated carbons. The second route is the copolymerization of vinylidene chloride monomers with vinylboronic acids. This will result in a diblock copolymer. This copolymer is then pyrolyzed resulting in a high-surface area, boron-doped carbon.

In Situ Visualization and Theoretical Modeling of Early Stages of Oxidation of Metals and Alloys

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Funding:	$150,000

When exposed to an oxidizing environment, nearly all metals except Au will develop a surface oxide phase that is commensurate with the imposed thermodynamic conditions. Fundamental understanding of the oxidation of metals has been the basis for a wide range of technological processes including corrosion, heterogeneous catalysis, fuel reactions, electrochemistry, and thin film processing. The challenge in the study of metal oxidation is to identify and then control the atomic processes governing the interfacial reactions of metal-oxygen, metal-oxide and oxide-oxygen at the different reaction regimes and scales. The objective of this program is to address these issues by studying the reaction from the initial oxidation stage of oxygen surface chemisorption to bulk oxide formation. To achieve this goal, in situ microscopy and spectroscopy techniques are utilized to monitor, in real time and at the atomic and nanometer scales, the surface oxidation of a number of model systems of metals and alloys. Such atomic in situ experimental data feed into the density-functional theory (DFT) modeling for identifying the critical kinetic and thermodynamic factors controlling the interfacial processes of metal oxidation under the technological relevant reactive environments. Four research thrusts have been pursued: (1) atomic structures of oxygen chemisorbed metal surfaces under realistic gas conditions, (2) precursor to the onset of bulk oxidation, (3) step-edge induced oxide growth, and (4) transitions from epitaxial to non-epitaxial nucleation of oxide islands. The study has provided unique and critical data of oxygen-metal reactions in a wide pressure and temperature range needed for a fundamental understanding of the atomistic processes governing the transition from oxygen surface chemisorption to bulk oxide growth.

Synthesis and Properties of Nanostructured Exotic Superconductors

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Superconductors are materials that conduct electricity with no resistance, i.e., no energy dissipation. In future electrically activated nanodevices, the use of superconducting interconnects is highly desirable, since it circumvents the damaging heat produced by energy dissipation in normal nano-conductors whose high resistance is inversely proportional to its cross-section area. Furthermore, the wave functions of the charge carriers - Cooper pairs will be strongly modified in a superconductor when they are squeezed into a small volume comparable to the coherence length or penetration depth; their wave functions will be strongly modified. Thus, superconducting nanostructures provide unique platforms to investigate and discover novel superconducting phenomena in confined geometries.

Funded by DOE, we have been developing methods to synthesize a new class of free-standing 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, which in crystal and thin film forms had been intensively studied and employed in single-photon detectors and other devices. Four-probe resistive measurements on individual $NbSe_2$ and NbN nanostructures revealed intriguing superconducting properties. The synthesis approach we developed consists of two-steps. Ffirst, to synthesize non-superconducting nanowires and nanoribbons of a compound ($NbSe_3$), which promotes anisotropic growth due to its unique crystalline structure; and second, to 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. This conversion approach can be applied to change the physical properties of existing compound nanostructures, enabling significant expansion of the availability of nanostructures with desired functions for potential applications.

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 have 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 system 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.

Three-Dimensional Evolution of Dendritic Mixtures

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Funding:	$374,000

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. The experiments will also serve as a test of simulations of the coarsening process and the theory, as well as to provide initial conditions for the simulations. 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.

Conduction Mechanisms and Structure of Ionomeric Single-Ion Conductors

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Funding:	$445,000

We have assembled an active team of scientists to study conduction mechanisms in ionomers. Our focus is on model systems that allow systematic variations in polarity, solvating ability, anionic group, alkali metal counterion and ion content.

The first system is in some sense the benchmark – sulfonated ionomers based on poly(ethylene oxide), whose ether-oxygens solvate cations, preventing the large-scale microphase separation of ions from the rest of the polymer that limits ion conduction in conventional ionomers. This allows modest conductivity but the cation motion is then coupled to the segmental motion of the polymer and limited by the glass transition temperature. Our entire team is actively studying these PEO-sulfonate ionomers using the full complement of materials characterization methods available to probe the ionic structure and mobility. We are now 2.5 years into this study and in the next few years we should develop a clear picture of the states cations are in and their conduction mechanisms in this class of materials.

Our second system, based on very low-Tg polysiloxane backbones, offers considerably more versatility in polar groups, solvating groups and anions that can be attached as side groups. In particular, we have identified some large bulky borate anions with very diffuse charge, which offer substantially lower binding energy to small cations like Li^+. Our team will first study this class of ionomer in an exploratory mode, simply to identify combinations of anion and polar solvating groups that warrant further investigation. If successful, our fundamental study should lead directly to improved models for cation motion in soft low-Tg ionomers and how that motion is facilitated by changes in charge density, dielectric constant, solvation and cation-anion pair energy. As very similar materials are being considered for advanced batteries, fuel cells, actuators, sensors and super-capacitors, our study of model ionomeric materials should aid in designing superior membranes in these arenas. The fact that ionomers only have a single mobile ion makes them ideal for studying conduction mechanisms but it is important to note that these ionomers are not intended to be candidate materials for actual battery applications.

To accomplish these goals we have assembled a team consisting of five faculty members. Ralph Colby (Materials Science, PSU) has considerable experience with synthesis, dynamics and charge transport in ionomer melts and polyelectrolyte solutions. Janna Maranas (ChemE, PSU) brings MD simulation expertise and calibration of simulations using quasielastic neutron methods and her force fields have been fully tested for PEOionomers. Karl Mueller (Chemistry, PSU) is an expert on multinuclear NMR methods, vital for probing ion surroundings and ion diffusion. Jim Runt (Materials Science, PSU) uses dielectric relaxation spectroscopy to study ionomers, with methods developed to extract conducting ion content and mobility. Karen Winey (Materials Science, UPenn) is a world-class expert on characterizing morphology of ionomers using SAXS and STEM.

Forces, Crystallization, and Assembly in Nanoparticle Suspensions

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Funding:	$134,000

Our work focuses on understanding colloidal forces and assembly, as well as structural transformations of (colloidal) nanoparticles using a variety of different theoretical approaches, ranging from first-principles density-functional theory (DFT) to classical molecular dynamics (MD) and Monte Carlo (MC) methods. Achieving controlled synthesis of colloidal nanomaterials with selected shapes and sizes is an important goal for a variety of applications that exploit their unique properties. In the past decade, a number of promising solution-phase synthesis techniques have been developed to fabricate various nanostructures. A fundamental understanding of the phenomena that promote selective growth and assembly in these syntheses would enable tight control of nanostructure morphologies in next-generation techniques.

In the past year, we investigated two aspects that underlie the shape-controlled synthesis of nanomaterials. In the first of these, we used classical MD simulations to study the role played by solvent in promoting anisotropic growth of colloidal nanostructures. Considering the growth of Ag nanowires and nanoplates in organic solvent, we studied how solvent influences the aggregation of a small and relatively isotropic nanocrystal with a larger nanowire or a square nanoplate. The two nanocrystals almost always adopt a mesocrystal configuration, a free-energy minimum in which the two particles hover next to each other with one or two layers of solvent between them -- analogous to experimentally observed mesocrystal structures. Nanocrystal aggregation occurs from the mesocrystal state and the free-energy barrier for aggregation is smallest on the smallest facets, which perpetuates anisotropic growth. These studies indicate that solvent can play a key role in promoting the anisotropic growth of colloidal nanostructures.

We also probed the interactions leading to surface-sensitive binding of polyvinylpyrrolidone (PVP), a well-known structure-directing agent in the synthesis of metal nanocrystals with controlled shapes, to Ag surfaces. We used first-principles DFT to identify several different binding states for PVP segments on Ag(100) and Ag(111) and found an energetic preference for Ag(100), which arises from a surface-sensitive balance between direct binding and van der Waals attraction. At the chain level, correlated segment binding leads to a strong preference for PVP bind to Ag(100). Our study underscores differences between small-molecule and polymeric structure-directing agents.

We studied the anatase-to-rutile transformation of titania nanocrystals. An important advance is our development of a local order parameter to distinguish anatase from rutile and intermediate anatase (112) twins at the resolution of a single TiO_2 unit. We applied the local order parameter and simulated X-ray diffraction in direct MD simulations of various anatase nanocrystals, as well as nanocrystal aggregates, to probe the transformation to rutile. The anatase-to-rutile transformation originates at surfaces and interfaces, where alternating anatase (112) twin planes form. Rutile nuclei form via transformation of anatase (112) twins and they grow rapidly when they reach a critical size that can be as small as 10 TiO_2 units. Rutile nucleii tend to have planar structures bounded by (101) surfaces and the ease with which they form is dependent on the structure of the nanocrystal.

Finally, to facilitate studies of aqueous titanium dioxide nanoparticles, we developed a force field for the interaction of molecularly and dissociatively adsorbed water with surfaces of titanium dioxide. We tested the force field by computing binding energies and conformations for molecular and dissociative adsorption on the major surfaces of anatase and rutile for various water surface coverages. We also used MD simulations to obtain density profiles and statistics of hydrogen bonding for water monolayers and bilayers adsorbed on anatase (101). All results were in good agreement with experiment, DFT, and/or ab initio MD simulations.

Giant Electrocaloric Effect In Ferroelectric Polymers With Tailored Polar-Nanostructures

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Recent research works from our group have demonstrated that giant electrocaloric effect can be obtained in the normal ferroelectric P(VDF-TrFE) copolymer and relaxor ferroelectric polymers. Moreover, we also showed that the defects modification in ferroelectric materials has the promise of further enhancing ECE. Proper defects modifications can significantly reduce the polar correlation and increase the number of polar-entities beyond that allowed by the macroscopic symmetry of the crystal structures, both of which will result in larger entropy change between the dipolar-ordered and disordered states.

In this renewal program, we propose to investigate ECE in the normal ferroelectric P(VDF-TrFE) copolymer over broad compositions. Since the dipole moment of VDF is twice of that of TrFE, increasing VDF/TrFE ratio will lead to larger entropy change between the dipolar ordered and disordered states and first order FE-PE transition. We will systematically investigate ECE in the defects modified P(VDF-TrFE) copolymers, especially on how the ECE evolves as the defects content increases and as the polymer is gradually transformed from normal ferroelectric to relaxor ferroelectric and eventually to a regular dielectric (non-ferroelectric). We also propose to investigate ECE in PVDF based ferroelectric nanocomposites. Combining these studies with the molecular, nano- and micro-structures, we would like to develop understanding of how various parameters in a ferroelectric polymer influence the electrocaloric effect and how to achieve very high electrocaloric effect in polymeric materials. This work will open up a totally new research area – developing polar-polymers with giant ECE, which have the promise of realizing high efficiency and environmentally friendly solid state cooling devices.

Hydrogen Caged in Carbon-Exploration of Novel Carbon-Hydrogen Interactions

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Funding:	$340,000

Hydrogen trapped in a carbon cage, captured through repulsive interactions, is a novel concept in hydrogen storage. Trapping hydrogen via repulsive interactions borrows an idea from macroscale hydrogen storage (i.e., compressed gas storage tanks) and reapplies these concepts on the nanoscale in specially designed molecular containers. Under extreme conditions of pressure carbon is expected to restructure to minimize volume via a mixed sp2/sp3 hydrogenated state. In the past year, we have been developing techniques to compress polyaromatic hydrocarbons in the presence of gases, in order to assess whether extreme conditions may trap gases via repulsive interactions. Materials are compressed in a diamond anvil cell with simultaneous characterization via multiwavelength in situ Raman spectroscopy to probe carbon-hydrogen interactions and structural changes in the carbon backbone. Typically, the aromatic or polyaromatic ring system will polymerize to form an extended reactive amorphous carbon networks under high-pressure, which has been demonstrated for benzene, naphthalene, anthracene, and pentacene in parallel work. We are currently working to extend these studies to include carbon transformation in the presence of H_2. We are also probing the polymerization of trypticene and hydrogenated fullerenes; the former provides a pre-existing three-dimensional backbone while the latter includes initial curvature, both of which are expected to be favorable for cage formation. For comparison, we are probing the penetration of H_2 in preformed carbon networks at extreme pressures. Complementary first-principles materials theory is being used to examine candidate carbon-cage structures and to predict the characteristic Raman signatures of hydrogen held in place by either repulsive interactions (caged hydrogen) or attachment to the carbon backbone in mixed sp2/sp3 states.

Development of in situ spectroscopic measurement techniques capable of combined high-pressure and variable temperature measurements has allowed us to explore other carbon-hydrogen interactions that are unresolved and debated in the literature. One such carbon-hydrogen interaction of particular interest is the binding mechanism between hydrogen and a carbonaceous support in the presence of a noble-metal dissociation catalyst (i.e., the hydrogen spillover mechanism). Incorporation of a catalyst into nanoporous materials has led to several reports of particularly high hydrogen uptake at room temperature and pressures less than 100 bar, but the results are contested, reproducible by only a fraction of laboratories, and any active sites on the nanoporous support that bind reversibly with spilled-over atomic hydrogen remain unclear. We have investigated the local interaction between atomic H and the graphite basal plane adjacent to a Pt dissociation catalyst with in-situ Raman spectroscopy and complementary density functional theory (DFT) calculations. These results provide spectroscopic evidence for hydrogenation of the carbon basal plane via the spillover mechanism; the feature is reversible for spillover to curved and defected activated carbon and irreversible to graphene. These results clarify whether H is chemisorbed or physisorbed, and how carbon structure and metal-carbon contact dictate the degree of reversibility.

Low-Temperature Synthesis Routes to Intermetallic Superconductors

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This project applies our expertise in the low-temperature chemical synthesis of alloys, intermetallic compounds, chalcogenides, and metal carbides to potential new advances in the field of superconductivity as well as, through more recent work, solar energy conversion. Our general modus operandi is to (a) develop new chemical methods for accessing solids under conditions that differ significantly from traditional routes, with the goal of discovering new materials, (b) expanding capabilities in the predictable synthesis of advanced colloidal nanostructures, with an emphasis on non-traditional systems that present fundamental chemical challenges that must be addressed, and (c) explore chemical and biological routes that will facilitate both large-scale colloidal synthesis and the purification of mixtures of colloidal nanostructures.

Four especially significant results emerged from this research during the past year, with additional advances that are imminent. First, we developed a new chemical approach for fine-tuning the compositions and phases of metal chalcogenide nanomaterials. This chemistry exploits the strong interaction between a phosphine and a chalcogen (e.g., S, Se), such that 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. One area where this chemistry is particularly useful is in facilitating subtle composition control in the superconducting PbO-type FeSe system, where the properties are known to depend sensitively on stoichiometry. Second, we recently synthesized a previously unreported family of binary Au$_3$M (M = Fe, Co, Ni) intermetallic compounds as nanoparticles, and our recent investigations taught us how these phases form in solution so that we are better poised to rationally target other non-equilibrium phases in the future. We also learned how to scale up the product yield by an order of magnitude and to minimize impurities, and these advances allowed us to characterize, for the first time, the magnetic properties of these materials, which are all either paramagnetic or superparamagnetic with low blocking temperatures. Third, we applied our expanding knowledge of colloidal routes to nanoscale metal borides and carbides, developed during previous years of this project, to the controversial colloidal nickel carbide system. There is disagreement in the literature about whether some colloidal routes to nickel nanoparticles yield the metastable hexagonal close packed (hcp) allotrope of elemental nickel, or whether these materials are better described as hexagonal nickel carbides (Ni$_3$C). We were able to synthetically tune through a Ni$_3$C1-x solid solution of isomorphous particles, and this allowed us to establish composition-structure-property correlations as a function of carbon content. Our results bridge previous reports of both hcp-Ni and Ni$_3$C and help to unify the literature in this area. Finally, we began focusing on narrow bandgap chalcogenide semiconductors comprised of earth abundant and low-toxicity elements, relative to those most commonly used for such purposes (e.g., Cd, Pb, Hg). We first reported colloidal germanium chalcogenide nanosheets (GeS, GeSe) as viable potential materials for visible light absorbers in solar cells. We then shifted to tin chalcogenides and learned how to precisely tune the thicknesses of laterally uniform and photoactive SnSe nanosheets. The SnSe nanosheets form by nanoparticle coalescence, first lateral then vertical, and this two-step approach provides important insights into how chemical routes can be used to precisely tailor the morphologies of two-dimensional nanostructures.

Electric-Loading Enhanced Kinetics in Oxide Ceramics: Pore Migration, Sintering and Grain Growth

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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 (YSZ), a widely used electrolyte material for solid oxide fuel cells and solid oxide electrolysis cells, with an emphasis on grain growth, second phase migration and sintering, under a large electric current density. Other prominent fast-oxygen oxide ceramics of current interest for oxygen and proton fuel cell applications will also be studied.

Fundamental Experimental and Theoretical Studies on a Novel Family of Oxides Catalyst Supports for Water Electrolysis

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Funding:	$250,000

Noble metals and their oxides (e.g., IrO_2 and RuO_2) are well known for their excellent electro-catalytic activity for use in proton exchange membrane (PEM) based water electrolyzers to generate clean hydrogen using the electric current generated from renewable energy (wind, solar, geothermal and hydropower). However, the cost of noble metals makes it imperative to search for stable catalyst supports to minimize the noble metal oxide loading while also enhancing the electro-catalytic activity and durability. The present project is directed at conducting fundamental experimental and theoretical studies to identify and synthesize more economical, more durable nano-structured electro-catalyst supports allowing substantial reduction of the noble materials while maintaining high electrocatalytic activity similar to that exhibited by the pure noble oxides. A convenient approach to reduce relative amount of expensive noble metal catalyst loading, such as IrO_2 is to generate a solid solution of this oxide with SnO_2 and transition metal oxides such as Nb_2O_5 or Ta_2O_5. Also, doping with fluorine and other elements may improve the electronic conductivity of the compound thus increasing the overall catalytic activity.

(1) During FY 2011, a series of materials comprising $(Ir,Sn,Nb)O_2$ and $(Ir,Sn)O_2$:F with IrO_2 content of only 20-25 at% were identified which demonstrate electrochemical activity almost identical to that of pure IrO_2. This indicates the promising nature of introducing SnO_2 and transition metal oxides, such as Nb_2O_5, which have the ability to exhibit multiple oxidation states, thus offering the opportunity to improve the electronic conductivity while also maintaining the chemical stability as shown by the initial and continued theoretical studies conducted in the research project. To elucidate the fundamental reasons contributing to the excellent electrochemical activity of the materials with very low noble metal content, a theoretical component of the present project has been established and conducted accordingly. During Year 2 of the project $Ir_{1-2x}Sn_xNb_xO_2$ and $Ir_{1-y}Sn_yO_2$:F with x=0-0.375 and y=0-0.75 have been chosen for investigation of the bulk and surface electronic properties. Calculations of the electronic structures of the compounds revealed strong correlation between Ir d-band center position and the catalytic activity demonstrated by the material. Such a correlation is conditioned by the complex hybridization of electronic Ir d-states and corresponding states of Sn, Nb and O during formation of the solid solution of binary or ternary oxides.

(2) There is a large family of niobates and tantalates of different divalent metals, such as Ca, Mg, Sr, Sn, Ba, Zn, and Cd, demonstrating high electrochemical stability but poor electronic conductivity. Doping of such oxides with elements from 3A, 3B, 5B, 6A, 7B group of the Periodic table may also improve the electronic conductivity while maintaining the high electrochemical stability. During Year 2 we selected the most structurally stable system Ca-(Nb or Ta)-O for our investigation. The theoretical study conducted showed that introduction of small amounts of 3A, 5B and 7B-group elements noticeably improves the conductivity in comparison to the elements from groups 3B and 6A of the Periodic Table. Also, a comparison of the cohesive energies calculated for the pure and doped oxides displayed Y doped $CaTa_2O_6$ to be the most stable compound among all materials considered in the study.

Future plans will consist of conducting an *ab-initio* study of the electronic structure, bulk and surface properties of pure Nb_2O_5, and Ta_2O_5 combined with doped structures containing small amounts of F, Nb, Ta, As, Sb, Bi, Cr, Mo, and W. Particular attention will be given to the investigation of the surface stability in the presence of sulfuric acid, which is the preferred electrolyte and the catalytic reaction mechanisms providing key answers to the scientific questions pertaining to the potentially promising electrochemical performance of these novel materials. The experimental component of the study will be focused on the fundamental science of development of new materials and the synthesis pathways to achieve these systems comprised of reduced noble metal catalyst loading. These fundamental studies will be conducted with the primary aim of correlating the synthesis procedures with the theoretical computational studies to gain a fundamental understanding of the improved catalytic activity of the various compositions with reduced noble metal contents. The basic science study conducted will provide key information that will be useful in the design of improved catalyst and catalyst supports for water electrolysis.

Optimizing Interaction Potentials to Form Targeted Material Structures

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This project seeks to develop a systematic 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. 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 desirable performance characteristics.

Integrated Growth and Ultra-Low Temperature Transport Study of the 2nd Landau Level of the Two-Dimensional Electron Gas

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Funding:	$100,000

We study the states of the second Landau level of a two-dimensional electron gas, corresponding to Landau level filling factors between 2 and 4. 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 Landau level filling factor 5/2 may result from an unusual pairing mechanism of the composite fermions described by the Pfaffian wavefunction. Because the pairing is believed to be p-wave, the 5/2 state may resemble other condensed matter systems of current interest such as strontium ruthenate, certain fermionic atomic condensates, and the quantum liquid He-3. Moreover several odd denominator fractional states in the second Landau level such as the 2+2/5 and 2+6/13 are quite distinct from their well understood lowest Landau level counterparts.

The study of the 5/2 state has been reenergized with the prediction that its excitations obey exotic non-Abelian statistics. The 5/2 and other novel states in the second Landau level are not only of fundamental interest as they may manifest behavior not seen in any other physical system, but also may find technological utility in fault-tolerant schemes for quantum computation. These exotic states are, however, fragile and hence they develop only in the highest quality GaAs host crystals and typically only at the lowest electron temperatures.

Building on a recently established combination of expertise and infrastructure at Purdue University, we will carry out an integrated growth and experimental study of the two-dimensional electron gas in GaAs in the second Landau level. Studies of the dependence on the disorder of the states of the second Landau level are expected to offer insight on the nature of these states and are currently under way.

Since the beginning of our DOE grant, 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, therefore, proven the collective nature of the reentrant integer quantum Hall states. Our manuscript resulting from this work is online at arXiv:1110.4121 and has been editorially approved for publication in *Physical Review Letters*.

The Dawn of Boron Fullerenes: Key Issues of Stability and Synthetic Routes

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Funding:	$250,000

During this period we have intentionally applied a “diversified” approach that is not only focused on the boron fullerenes family but also on exploring other potentially important boron-containing nanostructures. Presently our view is to broadly research the entire B-C-N triangle, while keeping a focus on boron-dominated nanostructures and their outstanding properties. We keep constant exchange between the experimental and theoretical groups, discussing the results and ideas, even when the specific objects of current experiment or computation are not identical.

Boron nanostructures, if systematically produced, would open a variety of opportunities. B-fullerenes, similar to C60, or the filled-solid clusters, must lead to a branch of chemistry with its own novelties; B-nanotubes (BT) should possess electronic properties beneficially more uniform than their carbon analogues. A systematic study of stability and investigation of possible ways of synthesis for boron nanostructures is critically timely. While theory has predicted some possibilities, the actual experimental evidence is so far rather sparse. The experimental report on BT remains rather more stimulating than conclusive. Theoretical models are being developed for the assessment of possible structures and properties, along with a series of experimental synthesis trials and characterization, including in our scope: hollow fullerene-type clusters, B-tubes, mono-atomic B-sheets—analog of graphene monolayer. Beyond the mono-elemental nanostructures, the chemical combinations of B with its neighbors in the periodic table (N, C) bring additional control in the synthesis and new rich functionality.

Atomistic Structure, Strength, and Kinetic Properties of Intergranular Films in Ceramics

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Thin (~1-2nm) rare-earth-containing silicate glassy intergranular films (IGFs) present between the grains in high strength-high temperature structural ceramics occupy only a small volume percent of the bulk material but can significantly influence mechanical, chemical, and optical properties. Because of their amorphous and thin nanoscale nature, understanding the atomistic basis for how these IGFs affect material properties has been experimentally elusive. Under DOE-BES support, we have been employing molecular dynamics (MD) computer simulations to describe the atomistic structure and dynamic behavior occurring in silicate IGFs in both oxide and nitride structural ceramics. The results of our simulations led to predictions of the effect of the crystal interface on the structure and composition within the IGF as well as on the locations of specific additive ions in the IGF. These predictions were eventually verified after the development of the most advanced electron microscopies: aberration corrected high resolution TEM and high angle annular dark field scanning transmission microscopy (HAADF-STEM).

We have since moved on to study the behavior of rare earth (RE) additives in the silicate-rich IGFs that were the focus of the most recent HAADF-STEM studies that showed the location of RE ions at specific sites on the prism surface of silicon nitride, with the locations varying as a function of RE additive. We reproduce the experimentally observed locations of La ions at the surface (which are similar to our earlier predictions using other additive cations), but more importantly, we have shown the complementary behavior of how this RE siting is affected by the concentration of specific anions in the IGF as well as how the RE ion causes a change in the location of anions in the IGF, both of which affect local composition that affect crystal growth and fracture behavior. Our simulations provide the energetic driving force for the distribution (segregation) of different species in the IGF.

By evaluating the change in the distribution of specific species within the IGF and at the IGF/crystal interfaces, we have been able to show how fracture stress is modified. Continued MD simulations using different RE ions are providing us with new insight into why previously published ab-initio calculations from other groups could not reproduce the experimentally observed location of Lu rare earth ions on the prism surface of silicon nitride. We have initiated ab-initio calculations to verify our MD simulations that are showing the correct locations of the Lu ions, consistent with the HAADF-STEM studies.

By understanding the differences at the atomistic level among the different RE ions on material behavior, we will potentially be able to provide replacement compositions that will maintain the integrity of these high-temperature high-strength ceramics.

Our simulations are being done in conjunction with experimental verification in collaboration with Dr. Pennycook at ORNL and Professors Phil Batson and Fred Cosandey at Rutgers, as well as interactions with Dr. Christoph Koch at Max-Planck Institut für Metallforschung, Stuttgart.

A Fundamental Study of Inorganic Type II Clathrate Open-Framework Materials

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The synthesis of new and novel materials is essential for the scientific progress and long-term technological growth of the U.S.A. New processing and crystal growth techniques are of keen interest towards this goal since for many materials of technological interest, as well as materials that probe fundamental new physical phenomena, the preparation of high-quality single crystals by traditional techniques is especially challenging. We employ two newly developed methods for crystal growth in the investigation of intrinsic structural, transport, and optical properties of intermetallic clathrates and other "open-framework" (cage-like) materials in order to develop fundamental structure-property relationships that expand the knowledge base of unique properties that arise from these materials.

These two crystal growth techniques, utilizing spark plasma sintering for crystal growth and the slow, controlled removal of alkali via vapor phase intercalation of graphite, were developed under the current DOE project and allow us to grow single-crystals of intermetallic clathrates of different compositions as well as new "open-framework" materials. In addition, the rich variety of compositional variations in clathrate materials represents an ideal material system to investigate the fundamental properties of Si, Ge, and Sn in novel crystal structures and bonding schemes.

The intellectual merit of investigating this material system is very closely tied with its novel structure and the corresponding physical properties it exhibits. The research into these unique properties can only be uniquely investigated in these materials. This work is intended to lead to a clear understanding of the unique properties that define the suitability of these materials for energy-related applications. This work will therefore have an impact on the development of technologically significant applications in power-conversion technologies (such as photovoltaics and thermoelectrics) and energy storage (lithium-battery technology).

Studies of Surface Reaction Mechanisms in Atomic Layer Deposition

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Funding:	$200,000

Atomic layer deposition (ALD) promises to be an enabling technique for creating the innovative nanostructured materials needed for future applications, including those in solar energy and photoelectrocatalysis. However, molecular-level knowledge of ALD mechanisms is generally poorly known. In this project, we perform studies to uncover molecular level mechanisms and nucleation processes active during ALD. A combination of in-situ and ex-situ spectroscopies together with modeling studies are being employed. Our recent activities have included studies of Pt, Ru and TiO_2 ALD. We have analyzed and modeled the nucleation process in Pt ALD using discrete nucleation sites formed by intentionally deactivating the Si substrate using organic self assembled monolayers (SAM). Recent studies have also examined the effects of TiO_2 microstructure on Pt nucleation by ALD. We have shown that for the same number of Pt ALD cycles, the Pt surface coverage depends on the thickness of the underlying TiO_2. Further studies have identified a strong dependence on the microstructure of the TiO_2 substrate which causes the observed thickness behavior. Specifically, studies revealed that continuous growth of ALD Pt occurs on anatase TiO_2 whereas island growth occurs on amorphous TiO_2. These results indicate that Pt nucleation is significantly affected by the microstructure of TiO_2 and provide insight into initial growth during metal ALD and the effects of surface structural properties on ALD nucleation. Work is also being carried out to develop systems for in-situ spectroscopic studies of ALD, using both laboratory-based and synchtrotron-based measurements. These in-situ analytic systems are currently being applied to studies of metal ALD.

Novel Theoretical and Experimental Approaches for Understanding and Optimizing Hydrogen-Sorbent Interactions in Metal Organic Framework Materials

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Funding:	$360,000

The aim of this program is to develop a fundamental mechanistic understanding of the interaction guest molecules (e.g. H_2, CO_2, N_2, 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), to study a number of different MOF materials. One of the goals is to provide insight for the role of unsaturated metal centers or active sites grafted to ligands in enhancing molecular uptake, selective adsorption and diffusion. The short term impact of the proposed 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 and selectivity.

This past year, we have synthesized and characterized a highly flexible and porous metal organic framework material, $Zn_2(bpdc)_2(bpee)$, where bpdc = 4,4'- biphenyl dicarboxylate, and bpee = 1,2-bis(4-pyridyl)ethylene, that exhibits remarkable capability to selectively capture and separate carbon dioxide from other small gases, including N_2, H_2, CO, O_2, CH_4, and H_2. Single component gas adsorption experiments yield a separation ratio of 294 for CO_2/N_2 at 0.16 atm and 25°C. For a gas mixture that mimics flue gas conditions (with a feed concentration of 20% of CO), a maximum separation ratio of 84 was obtained for CO_2/N_2 at 50 ºC. To the best of our knowledge, both values represent the highest CO_2/N_2 separation ratios reported to date. In addition, the single component gas separation ratios are calculated to be 190, 257 and 441 (v/v) for CO_2/H_2, CO_2/CH_4 and CO_2/CO at 0.16 atm, and 768 (v/v) for CO_2/O_2 at 0.2 atm, 25°C, respectively. Furthermore, the isotherms reveal that a breathing behavior with a pore opening is observed upon CO_2 adsorption at 0.1 atm, but not upon N_2 adsorption under similar conditions. Using Raman spectroscopy, we are able to detect substantial spectral variations that are associated with structural changes occurring during the pore opening (only for CO_2), which could explain the preferential adsorption of CO_2 over N_2. Using DFT simulations of ligand rearrangement (e.g. twisting), the observed Raman shifts could be related to twisting of the bpdc ligand, which represents a mechanism allowing the pore to open. The interaction of the CO_2 carbon center with the inter-ring C-C bond of this ligand is believed to be the origin of this twisting, which is possible because the type of connectivity of the bpdc (unidentate bonding) to the metal center is favorable for a rotation around this point. The bpee ligand can also accommodate the changes due to the C=C of the ethylene that changes length and accommodates these changes. Monitoring the C=C of the bpee ligand, we are able to extract information about the c-axes length with adsorption. This interaction is only possible for the CO_2 because of its larger quadruple moment (~4.3x1026/esu cm^2) as compared to N_2 (~1.52x1026/esu cm^2).

We have also functionalized bdc ligand in Zn(bdc)(ted)$_{0.5}$ by introducing hydroxyl and amino groups that lead to two new structures, Zn(bdc-OH)(ted)$_{0.5}$ and Zn(bdc-NH_2)(ted)$_{0.5}$, where bdc = terephthalate, ted = tryethylenediamine, bdc-OH = 2-hydroxylterephthalate, bdc-NH_2 = 2-aminoterephthalate. Zn(bdc)(ted)$_{0.5}$ can be considered a 3D porous structure having three interlacing 1D channels, while both Zn(bdc-OH)(ted)$_{0.5}$ and Zn(bdc-NH_2)(ted)$_{0.5}$ contain only 1D open channels as a result of ligand functionalization. A notable decrease in surface area and pore size is therefore observed in both compounds. Consequently, Zn(bdc)(ted)$_{0.5}$ takes up the highest amount of H_2 at low temperatures. Interestingly, both Zn(bdc-OH)(ted)$_{0.5}$ and Zn(bdc-NH_2)(ted)$_{0.5}$ show significant enhancement in CO_2 uptake at room temperature, however, suggesting that there are strong interactions between CO_2 and the functionalized ligands, and indicating that surface chemistry, rather than porosity, plays a more important role in CO_2 adsorption.

Our theoretical and experimental collaborative effort has made it possible to uncover H_2-H_2 interactions on neighboring sites in MOF-74, a prototypical MOF with unsaturated metal centers. Using the initial van der Waals Density Functional (vdW-DF) method developed earlier, we have shown that H_2 dipole moments and IR shifts should be greatly affected due to these interactions. By performing IR absorption measurements of H_2 in MOF-74-M (M= Zn, Mg) as a function of temperature and pressure [to 45 kTorr or 60 bars at 300K, and at lower pressures in the 20-200K range], we were able to detect these subtle but important effects.

We have also calculated the interaction of CO_2 in MOF74-Mg structures and found the primary CO_2 adsorption sites. We determine the frequency shift of vibrational modes of CO_2 when physisorbed in both Mg-MOF74 and Zn-MOF74. Surprisingly, we find that that the resulting change in shift is rather different for these two systems and we elucidate possible reasons. We explicitly consider three factors responsible for the frequency shift through physisorption, namely (1) the change in the molecule length, (2) the asymmetric distortion of the CO_2 molecule, and (3) the direct influence of the metal center. The influence of each factor is evaluated separately through different geometry considerations, providing a fundamental understanding of the frequency shifts observed experimentally.

Doping Cuprous Oxide in Electrolyte Solution: Dopant Incorporation, Atomic Structures and Electrical Properties

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Funding:	$167,000

This project pursues a fundamental study on 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 energy conversion devices, such as next-generation photovoltaic cells and photoelectrochemical cells. Cu_2O provides many advantages over current 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 PI's 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 proposal attempts to answer several fundamental questions about solution-based doping: Which dopants behave n-type and which behave p-type in Cu_2O? What solution-based chemistries incorporate the identified dopants into Cu_2O? How do the electrical properties (resistivity, carrier concentration, mobility, conduction type) change with doping?

The project involves both experimental and theoretical studies to answer these questions. Recent accomplishments in this project include demonstration of extremely large grains in Br-doped Cu_2O, understanding of the dependence of conduction type in Cu_2O on deposition pH, understanding of the electronic structures of several n-type dopants in Cu_2O, and an analysis on resource limitations to terawatt-scale photovoltaics.

Group IV Nanomembranes, Nanoribbons, and Quantum Dots: Processing, Characterization, and Novel Devices

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Funding:	$150,000

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, 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).

Atomic Layer Controlled Growth of Pnictide Thin Film Heterostructures by Design

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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. Recently, we reported novel template engineering using single-crystal intermediate layers of (001) $SrTiO_3$ and $BaTiO_3$ grown on various perovskite substrates. This has enabled genuinely epitaxial films of Co-doped $BaFe_2As_2$ with superior Jc of 4.5 MA/cm^2 (4.2K) and strong c-axis flux pinning. We also demonstrated low anisotropy $\gamma<2$, strong vortex pinning, a high irreversibility field H_{irr} (close to H_{c2}), and critical fields of H_{c2} well over 50 T.

Our advance in pnictide single-crystal film growth allows the design and control of pnictide superconducting films and heterostructures to probe the fundamental superconducting mechanisms of this unique class of materials. 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

(4) Pnictide grain boundary engineering

The proposed work is based on a new growth technique with the unique potential for pnictide heterostructure synthesis with atomic-level control. Scientifically, we will learn how atomic scale positioning of interfacial layers modify the growth modes, epitaxial arrangements, and strain states. Technologically controlled growth of pnictide thin films and heterostructures through interfacial engineering will lead to the discovery of new superconducting structures and devices. In addition, the template technique that permits high-quality pnictide films on oxide substrates will likely be useful in interfacing other metallic or semi-metallic systems with oxides.

Group IV Nanomembranes, Nanoribbons, and Quantum Dots: Processing Characterization, and Novel Devices

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Funding:	$470,000

Fundamentally a platform for new physical and chemical phenomena, extremely thin semiconductor sheets also offer possibilities for novel structures that may form the basis for devices relevant in energy harvesting, transformation, and conservation. Our work has been in Group IV-based nanomembranes (which we abbreviate as SiNMs), but the platform is extendable to other materials and a range of structures and functions, using the approaches we have developed. The platform of single-crystal semiconductor sheets offers the choice of nano-size in one, two, or three dimensions, as well as the formation of structures with mixed dimensions. The research, we believe, involves fascinating synthesis and processing science, excellent prospects for modifying and enhancing materials properties, and a number of technology drivers.

The novelty of SiNMs (and by extension other materials that can be grown heteroepitaxially and released from a bulk substrate, including other compound semiconductors, functional oxides such as piezoelectrics and ferroelectrics, and even metals) rests in several features. (1) They are thin; thinness brings many new phenomena. The very high interface-to-volume ratio makes surfaces or interfaces, and their chemical and structural properties, very important contributors to unique membrane electrical, thermal, and mechanical behavior. (2) They can be strained to a high degree, effectively allowing lattice constant choice. They can retain the perfect-single-crystal, dislocation-free nature of the original substrate after release to make them free-standing. Many of the most fundamental materials properties are influenced by the lattice and distortions of the lattice. (3) They are easily stackable and bondable, introducing an entirely new set of materials that change their properties vertically on the scale of 100nm or thinner. (4) They are patternable using standard top-down lithography methods, and can take on a large range of shapes by engineering the strain and the geometry. Thus all nanowire research (electronic and thermal transport, sensitivity to surface chemical modification, piezoelectricity, mechanical properties, …) is accessible, with much better defined structures than are obtained by conventional methods. Novel shapes (tubes, rolls, curved sheets, rings) bring an entirely new spectrum of properties and potential applications. (5) They are flexible and obviously transferable to foreign hosts, allowing on the one hand research into dislocation engineering and thus fundamentally new studies of dislocation and other defect formation and propagation, and on the other, flexible devices that have a wide range of applications.

The ongoing work focuses on the above five basic-property categories, enlarging and refining the effort of prior years, which has allowed us to visualize the vast extent of possibilities and has already achieved unique results. We believe the elegant nanoscience and obvious energy related technological potential will continue to have considerable impact also educationally and in terms of visibility among the public. It is expected that new patents will issue in the proposed grant period. We also believe that the proposed work addresses effectively all the scientific challenges of the Synthesis and Processing Core Area of the Division of Materials Sciences and Engineering of the Office of Basic Energy Sciences, as well as three of the five Grand Challenges described in the 2007 BESAC report.

The goals of our research are the following:

- Of the vast array of possibilities, choose research topics that we perceive as most likely to achieve out-of-the-box, innovative results in processing science.
- Focus this effort on the above five categories: thinness, strain, stackability, patterning, and flexibility.
- Develop and apply appropriate characterization methods and theory to quantify the outcomes of our synthesis and processing efforts, explain new phenomena, and predict behavior of prototype structures and devices.
- Focus on the following properties: 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.

Templated Bottom-up Synthesis of Semiconducting and Nanostructured Graphene Materials

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Funding:	$150,000

Graphene has received tremendous attention because of its exceptional properties, such as its ultrafast charge transport characteristics, excellent mechanical strength, flexibility, and resilience, as well as its outstanding thermal conductivity and its ultrahigh surface area/volume ratio. The nanostructuring of graphene further enhances its properties by altering its electronic structure, opening an energy gap resulting in semiconducting behavior, and increasing the accessibility of the surfaces and the edge density. The exceptional properties of nanostructured graphene materials have the potential to lead to advances in next-generation photovoltaic energy harvesting, energy storage, and semiconductor-based logic and sensing. These technological advances will be possible, however, only if the synthesis of planar nanostructured graphene materials can be realized with high quality and by rationally controllable means.

Traditionally, planar nanostructured graphene materials have been fabricated by growing continuous sheets of graphene and then etching the sheets into nanostructures, from the top-down. However, the top-down nanopatterning of graphene is severely limited by the etching tools that are available, which induce substantial defects, oxidation, and disorder. These defects degrade materials performance.

To overcome this challenge, we have developed a new strategy for the rational synthesis of patterned graphene from the bottom-up, called barrier-guided chemical vapor deposition (BG-CVD). In BG-CVD, graphene growth by CVD is laterally restricted on planar metal surfaces by selectively passivating the catalytic activity of the metal with patterned barrier templates designed to (1) locally limit the generation of atomic C species and (2) confine their migration.

We have specifically implemented BG-CVD 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 cm2. The BG-CVD materials are highly crystalline with domains > 4 microns and with edge-defect concentrations reduced by a factor of 2-10x compared to top-down etched samples from literature. Electrical transport measurements of graphene nanoribbon arrays (width = 25 nm) indicate high mobility (215 cm2/V/s).

In the future, it should be possible to realize large-bandgap semiconducting graphene materials via BG-CVD in combination with state of the art lithography with features of width < 10 nm, due to the method’s sub-1 nm pattern reproducibility. Ultimately, as BG-CVD avoids chemical etchants and instead relies on a self-limiting growth processes to abruptly define edges, we expect that this method will lead to graphene materials with superior performance.

Science of Heteroepitaxy for Energy-Efficient Lighting

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Funding: $170,000

Over the past two decades III-N heteroepitaxy has been carried out in largely an empirical manner. This proposal aims to establish a scientific and coherent model over a diverse range of heteroepitaxial phenomena occurred in III-N growth, from nucleation to coalescence, on a variety of crystallographic planes. A novel technique, differential selective area growth (Δ-SAG), is proposed as an accurate yet flexible method to monitor and record growth kinetics that determine the microstructural and morphological qualities. We also plan to demonstrate an active and effective control of the dynamic process of heteroepitaxy through the use of intrinsic and extrinsic morphactants, designed to alter the anisotropy of growth kinetics, to create new dimensions and a new paradigm in heteroepitaxial control that is at the heart of contemporary production of solid-state lighting devices.

DOE National Laboratories

Novel Materials Preparation and Processing Methodologies

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Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 5 Undergraduate(s)
Funding:	$1,632,000

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. Indeed, many of the major discoveries of condensed matter science during the last 50 years have been made possible by the discovery, growth, control, and modification of new materials. The design, synthesis, and characterization of new materials that lead to important discoveries, both expected and unexpected, as well as new knowledge and techniques, within and across traditional disciplinary boundaries, are critical components of the DOE-BES mission. Discovery and design of new materials is one of the key, cross-cutting research areas called out in every energy-related basic science materials challenge. In support of this mission, the Novel Materials Preparation and Processing Methodologies project strengthens the materials synthesis mission of Ames Laboratory through:

- quantifying and controlling processing-structure-property relationships of highly responsive materials (Fe-As based superconductors, magnetostrictive (Fe-X alloys) and ferromagnetic shape memory alloys (Ni-Mn-X alloys)
- advancing the ability to synthesize and characterize high purity, high quality novel materials, primarily in single crystal form, spanning a range of sizes, through identifying operating limits for growth by defining stable morphological growth regimes
- developing unique capabilities and processing knowledge in the preparation, purification, and fabrication of metallic elements and alloys
- providing high-purity, high-quality, and well-characterized materials in support of research programs at the Ames Laboratory and throughout the United States (and globally) at other government, academic, and private industrial laboratories
- exploring promising phase spaces (either physical or chemical) that we identify as compelling based upon advances in synthesis and/or control of novel materials

Structure and Dynamics in Condensed Systems

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Students: 6 Postdoctoral Fellow(s), 5 Graduate(s), 1 Undergraduate(s)
Funding: $2,198,000

The freezing of liquid metals and alloys provides accessible pathways to a rich and diverse spectrum of materials and structures with a wide range of properties and applicability. Indeed, the phenomenon of morphological selection during the growth of a crystalline phase from its melt is one where nanoscale interfacial mechanisms and microscale morphological effects act in concert with the longer range processes of thermal and chemical diffusion in response to the global forces which drive the overall freezing transformation. Moreover, driving these processes further from equilibrium can lead to new multi-scale structures along pathways involving highly undercooled metallic liquids, amorphous solids, and metastable crystalline phases. Effective navigation of these far-from-equilibrium dynamical landscapes, however, requires the resolution of several fundamental questions that have been longstanding barriers to advancement in this area. In this project, we seek to understand the most critical unresolved issues (i.e., the structure of liquids and the behavior of interfaces that govern the multi-scale dynamics under these far-from-equilibrium conditions). More specifically, our aims are to (1) quantify atomic-scale structure of metallic liquids and glasses, (2) identify the atomistic origins of interfacial properties and quantify their role in multi-scale structural dynamics, (3) incorporate the atomistic structure of liquids and glasses into appropriate solution-based models for the prediction of relative phase stability, and (4) predict phase selection and structural dynamics. With potential applications in magnetic, thermoelectric, and various other anisotropic coupled-response materials with diverse functionalities, the goal of this project is to establish the fundamental basis to enable the realization of new materials and new levels of structural control.

Molecular Beam Epitaxy of Complex Materials, Bulk Materials Synthesis and Characterization

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Students: 2 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: $2,187,000

Bozovic FWP: The mechanism of high-temperature superconductivity (HTS) is one of the most important problems in Condensed Matter Physics. Some basic facts—the dimensionality, the spin and the charge of free carriers, the nature of superconducting transition, the effective interaction that causes electron pairing—are still unclear. Our main goal is to perform experiments that shed new light on these key questions.

Petrovic FWP: The core research program concentrates on the synthesis and characterization of the new model materials of current interest in condensed matter physics. We put a strong effort in the discovery of new phenomena associated with the correlated behavior of electrons, superconductivity and magnetism. We currently pursue several interpenetrating research directions: Quantum criticality, Metal – insulator transitions (MIT) in nearly magnetic materials, Materials for thermoelectric and spintronics and Facility development.

Synthesis and Characterization of Individual Carbon and Perovskite Oxide

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Students: 0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding: $414,000

The ability to synthesize, functionalize, and purify novel nanomaterials and to understand their transport, optical, electrochemical, and mechanical properties lies at the forefront of current materials science research. The goal of this project is to understand the chemistry and physical properties in intriguing nanoscale materials systems, i.e., carbon nanotubes and nanoscale forms of non-carbonaceous nanostructures such as metal oxides, including perovskite materials.

Design and Synthesis of Nanomaterials

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Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $473,000

The objective of this program is to perform basic experimental and theoretical research that provides a new level of understanding of the mechanisms that control the organization of nanostructured materials during non-equilibrium to equilibrium transformations. The primary focus is the assembly and controlled synthesis of elemental and multi-component nanoparticles on surfaces by the destabilization of thin films. Specifically, this work investigates how intrinsic thermodynamic properties (micro- and nanostructure), thin film size, geometry and dimensionality, substrate composition, orientation and spatial inhomogeneity, and designed perturbations effect surface wave instabilities and homogeneous and heterogeneous hole nucleation. Furthermore, this project elucidates the subsequent energetic and transport regimes that are operative during the self and directed assembly in both the solid and liquid state. Finally, the resultant, and often times unique, nanoparticle properties are being measured. The fundamental understanding of this instability-induced organization process makes possible the directed synthesis and assembly of metal alloy nanoparticles with designed composition, structure, orientation and spatial arrangement. The knowledge gained regarding the controlled synthesis of such structures will help in the development of model systems for fundamental studies and functional materials related to energy applications (plasmonics, catalysis, sensors, etc.).

Growth Mechanisms and Controlled Synthesis of Functional Nanomaterials

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,063,000

The goal of this program is to develop a fundamental understanding of the non-equilibrium aspects of nanomaterial synthesis by exploring the growth mechanisms and resulting structures of nanoscale materials formed in controlled environments. Pulsed, non-equilibrium growth and processing approaches, such as those involving lasers and supersonic molecular beams, are developed to supply the necessary kinetic energy required to explore the synthesis of nanostructures with metastable phases and structures that are inaccessible using traditional synthetic methods. A distinguishing feature of the program is the development and application of time-resolved, in situ diagnostics of nanomaterial growth kinetics and a corresponding development of models to understand the underlying kinetic and chemical pathways. Spatial confinement and reactive quenching approaches are developed to explore the synthesis mechanisms of rationally-designed nanostructures with enhanced intrinsic properties, targeting (1) oxide, carbon, and alloy nanomaterials produced in metastable states by catalyst-free or catalyst-mediated processes and (2) doped, decorated, and filled nanomaterial hybrids designed to induce permanent electric fields or distribute charge within nanostructures. Theoretical methods are used to understand fundamental mechanisms of synthesis in order to guide the formation of nanostructures tailored to enhance energy storage, catalysis, thermal management, and photovoltaics in support of DOE's energy mission.

In situ Studies of Solid Electrolyte Interphase on Nanostructured Materials

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Funding:	$651,000

The overarching goal of this project is to develop a molecular level understanding of the growth mechanisms, structure, and dynamic properties of the solid electrolyte interface (SEI) for advanced electrical energy storage systems. To achieve this goal, we will first synthesize a series of model compounds that have defined structures to mimic the formation of SEI on electrodes and then study the dynamic properties of the SEI by using a combination of in situ characterization techniques including neutron scattering, transmission electron microscopy (TEM) and vibrational spectroscopy. The key questions to be answered by this investigation are the following:

(1) What governs the lithium-ion conductivity of SEI?

(2) How does the electrochemical cycling affect the chemical and physical structures of the SEI?

(3) How do the structure and composition of SEI alter into the electrochemical properties of the electrodes including electrochemical reversibility, thermal stability, and chemical compatibility with liquid electrolytes?

The outcome of the project will reveal the underpinning physics of the structural and dynamic properties of SEI and therefore guide the research on correlated materials for advanced electrical energy storage system with high energy and power densities that meet the requirements for grid-scale electricity storage and electrified transportation systems.

Electronic and Magnetic Properties of Doped Oxide Films

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$777,000

The broad range of electronic and magnetic properties exhibited by metal oxides can be extended by selective doping. By utilizing thin-film deposition under controlled conditions, well-defined doped oxide films and multilayers can be grown. We will utilize molecular beam epitaxy and pulsed laser deposition to synthesize novel doped oxides in several forms. These include near-perfect epitaxial films and layered structures of simple and complex oxides with uniform and spatially confined dopant distributions. The overarching goal is to create and investigate well-defined and well-characterized oxide structures in order to elucidate the effect of different doping schemes and crystallography on magnetic, electronic, and magneto-electronic properties. In addition to a multi-facetted experimental approach, we will employ state-of-the-art solid-state theoretical methods to predict structures, energies and magnetic coupling schemes in select systems, as well as to assist in interpreting experimental results. The proposed research will significantly deepen our fundamental understanding of doped oxides, as well as shed light on the feasibility of using magnetic oxides to advance the field of semiconductor spintronics.

Molecularly Organized Nanostructured Materials

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$650,000

Self-assembled materials with controlled nanostructures and functions have great potential for energy storage and conversion. Although many different approaches have been reported, there is a fundamental gap in the understanding of the underlining principles, in particular, the understanding and controlling the competing driving forces for crystal growth and three-dimensional self-assembly. The overall goal of this project is to investigate molecular-directed crystallization and self-assembly phenomena at the interfaces for synthesizing nanostructured materials with controlled micro- and nanoporosity, desired stable crystalline phases, and tailored multicomponent three-dimensional architectures. The project focuses on well-defined experimental systems, such as two-dimensional graphene building blocks, and explores the surface chemistry in order to develop new approaches to assemble complex materials using the 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. New in-situ transmission electron microscopy techniques will also be developed to obtain real-time kinetic information of nucleation, crystal growth and structural evolution. The electron and ion transport properties are measured by both microscopic and molecular spectroscopic methods, and correlated with the structure and surface chemistry of the materials. A multiscale model combining density functional theory and phase-field theory will be used to understand the coupled charge transport and the structure-property relationships.

The proposed research contains four subtasks: (1) molecular interactions at the interfaces, (2) fundamentals of nucleation and growth, (3) three-dimensional assembly of functional materials, and (4) charge transport and structure-property relationships.

Theoretical Condensed Matter Physics

Institutions Receiving Grants

Theoretical Investigation of Magnetization Dynamics at Elevated Temperatures

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Funding: $80,000

Laser-induced demagnetization (LID) and Heat Assisted Magnetization Reversal (HAMR) constitute a promising way to manipulate the magnetization direction by optical means. We have recently developed theoretical formulation for both LID and HAMR.

For LID, we considered demagnetization processes by explicitly taking into account energy and angular momentum transfers among electrons, spins and lattice. By properly treating the spin system in a self-consistent random phase approximation, we derive magnetization dynamic equations for the entire range of temperature. The dependence of demagnetization on the temperature and pumping laser intensity is calculated in detail. In particular, we show several salient features for understanding magnetization dynamics near the Curie temperature. While the critical slowdown in dynamics occurs, we find that the external magnetic field can restore the fast dynamics. A manuscript was submitted to *Physical Review B* in August 2011.

For HAMR, an equation that is capable of addressing magnetization dynamics for a wide range of temperatures is proposed. The equation reduces to the Landau-Lifshitz equation at low temperatures and to the paramagnetic Bloch equation at high temperatures. Near the Curie temperature, the magnetization reversal and dynamics depend on both transverse and longitudinal relaxations. Our proposed equation can be broadly used for modeling heat assisted magnetic recording. A manuscript was submitted to Phys. Rev. Lett. in October 2011.

Properties of Multiferroic Nanostructures From First Principles

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Funding: $150,000

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 (ME) 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. Therefore, they are key materials for actuators, sensors, and energy conversion and storage. They are specifically relevant to DOE's missions in energy efficiency, and transportation, conversion and storage technology.

Multiferroics, in their bulk and (thick) film forms, have been intensively studied in the last century, from the sixties to the eighties, then ``fell in disgrace'' among the scientific community (mostly due to weak ME coefficients) until recently experiencing a huge regain in interest. Consequently, an extensive understanding of multiferroic bulks and (thick) films has been gained and numerous breakthroughs have occurred. For instance, one better understands why so few materials simultaneously exhibit ferroelectricity and magnetism and how their magnetic ordering can be efficiently controlled by the application of electric fields along specific directions. Similarly, it is now clear that some multiferroics can possess a rather large electrical polarization.

On the other hand, little is currently known and/or deeply understood about multiferroic nanostructures -- e.g., ultrathin films, wires, nanotubes, and three-dimensionally confined multiferroic nanodots --, despite their technological promise in tuning towards a desired behavior that is not always achievable in a bulk-like material and despite their fundamental promise in yielding novel, exciting effects. As a matter of fact, the precise effects of the substrate, growth orientation, surface termination, thickness, electrical boundary conditions and dimensionality on the properties of multiferroic nanostructures are basically unknown.

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.

It appears 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 are confident that these insights can 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:	$91,000

This single-investigator grant supports the PI's research in theoretical condensed matter and materials physics. A large part of the research activities have been on electron systems where the correlation effects and their interplay with the breaking of translation symmetry due to disorder introduce new physics in the quantum electronic states that have not been understood previously. Recent activities focused on high temperature copper oxide superconductors, the multiorbital iron-based superconductors, and the fractional quantum Hall effects in graphene. Completed works include the construction and development of a valence bond glass theory for the pseudogap phase in high-Tc cuprate superconductors, a theory of superconductivity mediated by charge fluctuations in iron-based superconductors, and a composite Dirac fermion theory for the Abelian and non-Abelian fractional quantum Hall states in single-layer graphene.

Focused Research Center in Correlated Electronic Materials

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Students:	6 Postdoctoral Fellow(s), 8 Graduate(s), 3 Undergraduate(s)
Funding:	$100,000

The grant supports the collaborations among theory and complimentary experimental efforts (STM, ARPES, and Optics) at Boston College in one of the DOE Grand Challange areas of correlated electron and complex materials. The team has a track record of synergetic collaborations in the field of high-Tc cuprate and iron-based superconductors, sodium cobaltates, and strontium ruthenates. From 2010 to 2011, these collaborative research activities have led to seven published papers including two in *Nature Phy*sics, two in *Physical Review Letters*, and one in *Nature Communications*.

Recent research activities of the group have led to the observation of the three-dimensional (3D) superconducting gap function in optimally-doped iron-pnictide superconductors and the description of the measured gaps on all Fermi surfaces by a single 3D gap function that is consistent with the existence of only two dominate pairing energy scales, the in-plane and out-of-plane pairing strengths. This work points to a common origin for the pairing strength on all Fermi surfaces and provides the much needed insights for understanding the mechanism of superconductivity in Fe-based superconductors. The iron-pnictides are multiorbital systems where the electron correlation strength is intermediate and comparable to the kinetic energy. This intermediate interaction regime represents the challenge for understanding correlated systems as the electrons straddle between having predominantly itinerant and localized characters. The team's theoretical work revealed that nonperturbative correlation effects are essential to stabilize the metallic spin density wave phase with small magnetic ordered moments observed experimentally. For the high-Tc cuprate superconductors, the combined STM and neutron scattering experiments on optimal electron-doped PLCCO samples demonstrated the spatial coexistence of superconductivity and antiferromagnetism. Contrary to phase separation observed in some hole-doped copper-oxides, the AF order and the superconductivity are found to be inhomogeneous and compete locally on nanometer scales in electron-doped materials. The group has also initiated research efforts in the field of topological insulators. Recently accomplished works include the observation of broken time-reversal symmetry using combined STM and ARPES probes on the surface of magnetically doped topological insulators; and the discovery by STM of unidirectional stripes and the induced periodic modulations in the Landau level energies that raise the potential to realize 1D quantum wires using topological insulators.

Quantum Nanowire Multi-Connections

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Students: 0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: $114,000

This project focuses on a number of basic science questions pertaining to the behavior of correlated electrons at the junctions of multiple quantum wires, such as for example Y-junctions and cross-junctions. 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.

The Physics of Graphene

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Funding: $110,000

Graphene is the only known example of a metallic membrane that combines the unique properties 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 are particularly interesting because of its inherent strong quantum and thermal fluctuations that make many-body states such as superconductivity, magnetism, charge density waves (CDW), 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 in Interacting and Spin-Orbit Coupling Electronic Materials

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Funding: $110,000

The three main themes of the research carried out during the past year (2011) of the DOE support are as follows.

(1) Establish new fractionalized quantum phases without a magnetic field. We have been studying the interaction effect on various lattice models with spinorbit interaction, which can be realized either in condensed matter or optical lattice systems. By tuning the energy band dispersion for a class of models with nonzero Chern index (known as Haldane's model), we establish the fractionalized states in some simple lattice models with one near flat energy band. Our study led to the first theoretical discovery of the fractional quantum Hall effect (FQHE) and non-Abelian bosonic Moore-Read state without Landau levels. Our work has attracted wide attention and stimulated a lot of new researches. This line of research has led to two published and one submitted papers.

(2) DMRG development for FQHE and topological systems. We have developed DMRG codes for FQHE and other systems with topological order. We are able to access 5/2 FQHE systems with 34 electrons, which is about twice the system size studied using exact diagonalization (ED) method. We have also obtained full entanglement spectrum for the ground state, which can be used to determine the topological order of the system. We have one paper published and we are currently obtaining interesting results for graphene electron systems regarding the competition between the real spin and pseudospin magnetism, SU2 and SU4 fractional states and quantum phase diagram. In the lowest Landau level (n=0), we find interesting new quantum states at filling 4/3, where both spin and pseudospin form singlet state. This finding may help to understand experimental observations at fractional fillings of suspended graphene.

(3) Exact diagonalization calculations of quantum transport properties for disordered electron systems-- While the above DMRG calculations allow us to go to larger system sizes for interacting systems, ED still have some advantage as it can be used to determine various quantum transport properties in the presence of random disorder scattering. While we are developing DMRG based method for such study as well, we are currently studying the thermoelectric transports of Dirac fermions in graphene in the presence of strong magnetic field using ED. We have generalized our last year's study to bilayer graphene systems. We have obtained the universal behavior of the electric and thermoelectric transports for Dirac fermions with behavior of the electric and thermoelectric transports for Dirac fermions with short-range or smooth (Coulomb scattering from charged impurities) disorder scattering for unbiased system similar to monolayer graphene. The transverse thermoelectric conductivity reaches a universal quantum value at the center of each LL in the high temperature regime while it has a linear temperature dependence at low temperature. We contribute the universal behavior for both systems to the coexistence of particle and hole Landau levels around the Dirac point. When a finite interlayer bias is applied and a band gap is opened, it is found that the transport properties are consistent with those of a

band insulator. We have also compared our results with experiments and obtained very good agreement.

We have also carried out numerical studies of the quantum spin Hall effect (QSHE) with time-reversal symmetry (TRS) breaking Rashba interaction. Conventionally, the nontrivial topological properties are characterized by the Z2 index, which became trivial after breaking TRS. Here, we found that without TRS, QSHE persists and is characterized by a spin-Chern number. A topological phase transition from the TRS broken QSHE phase to a quantum anomalous Hall phase occurs at a critical exchange field, where the bulk band gap just closes. This work has established a new theoretical framework for studying the topological insulators with various symmetry broken perturbation.

To summarize, we have made substantial progress under the DOE support in the past year.

Semiconductor Nanostructures by Scientific Design

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The development of advanced materials is widely recognized as a key element for creating the new technologies required to provide adequate, clean energy for our planet. Research on materials for efficient and sustainable energy supplies is currently driven by experiment and much effort focuses on the search for nanostructured materials with targeted properties. However the increasing sophistication in manipulating matter at the nanoscale acquired by experimentalists and, to some extent engineers, calls for guidance and interpretation using detailed, microscopic theories. In addition, theoretical and computational tools with robust predictive power are needed, in order to design, in an efficient and innovative manner, novel materials for renewable energy applications.

Within the overarching goal of developing and applying predictive, microscopic simulation techniques to understand and design materials for energy applications, we focus on structural, electronic and optical properties of nanostructured systems. We aim at providing a first principle description of integrated materials, inclusive of surfaces and interfaces at the nanoscale, and in particular of assembly, embedding and solvation of semiconductor nanoparticles, so as to model realistic environments, directly comparable with experimental conditions.

We address three basic, scientific problems: (1) devise realistic structural models of nanostructured materials, for example nanoparticles embedded in solid matrices or immersed in a fluid; (2) provide an accurate description of all relevant interactions in a given, complex material, including weak forces within, e.g., self-assembled monolayers on surfaces (in particular dispersion forces, that in general are poorly understood); and (3) provide an efficient and accurate description of excited state properties of nanostructures, beyond standard Density Functional Theory, so as to understand and predict electronic properties relevant, for example, to solar conversion devices.

Theory of Oxide Nanostructures: Polarity, Dimensionality, and Strong Interactions

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Two dimensional “semi-Dirac” systems. Arguably our most visible accomplishment has been to introduce a new `state of matter’ into the field of condensed matter research. Graphene, with its linear Dirac-Weyl dispersion emanating from a point Fermi surface, has resulted in an incredible explosion of research and a Nobel Prize (2010) in physics. This system is an offshoot of the `zero-gap semiconductor’ in conventional systems, which also corresponds to a point Fermi surface. Both achieve the point Fermi surface due to symmetry of the lattice, though the graphene case is different and more dependent of the (hexagonal) lattice. In studies of ultrathin VO_2 layers confined to 2D behavior by confinement within (thicker, insulating) TiO_2 layers, we discovered the distinctive`semi-Dirac’ dispersion, in which quasiparticle dispersion is linear in one direction (Dirac-Weyl, like graphene) and quadratic (massive, conventional) in the perpendicular direction. Our designation of “semi-Dirac” has been accepted in the literature. Our original discovery [Pardo & Pickett, *Physical Review Letters* (2009)] has been followed in this review period by another high visibility paper [Simth et at., *Physical Review Letters* (2011)] providing a low-energy, tight binding model of how the unique dispersion arises, and providing basic results of low energy properties, and further buttressed by an archival publication [Pardo & Pickett, *Physical Review B (2011)*] describing much more about the VO_2/TiO_2 superlattice system that gave birth to this phenomenon, including effects of spin-orbit coupling and of interfacial mixing (neither of which destroys the unusual semi-Dirac dispersion). An extensive paper on more of the low energy properties of the semi-Dirac system is in preparation.

LAYERED NICKELATES

Our work on layered nickelates, which are bulk materials but are very strongly two-dimensional in their electronic behavior, began with $La_4Ni_3O_8$. This insulating compound is formally Ni(1.33+) and “should” be metallic. We established that, although the dispersion is strongly two-dimensional, there is important coupling in the z-direction between Ni d(z2) states (or Wannier functions). Density functional calculations, enhanced by local correlation effects, established that antiferromagnetic order is preferred within the Ni trilayer, which narrows the 2D bands considerably.

The remaining d(z2) coupling within Ni trilayers becomes crucial, and couples the three Ni ions in the trilayer into a “molecule.” Within this molecular subspace, strong interaction effects provides Mott insulating behavior, where the characteristic orbitals are not single-ion but instead are ‘molecular-like’ combinations of Ni ions in the trilayer. In this way, the non-half-filled Ni(+1.33) system can become Mott insulating. This new result was reported in *Physical Review Letters 105, 266402* (2010). The analogous $La_3Ni_2O_6$ system (Ni(+1.5)) behaves in an analogous manner (*Physical Review Letters* B 83, 245128 (2011)) and some analogous nickelates could also be understood in this way. A further manuscript elaborating on the spin-state transition of the Ni ion in these materials has been submitted for publication.

Polar oxide nanostructures. Our work, reported last year, on a “parallel electron-hole bilayer” for ultrathin layers of $LaAlO_3$ on $SrTiO_3$ has received much attention and several invited talks by the two senior principal investigators. We have followed up by studying the effects of metallic contacts (overlayers, on top of the $LaAlO_3$ layer). A surprising result is that in all three cases studied (Ti, Al, Pt) the contact layer counteracts the internal field within the $LaAlO_3$ layer, and there is no impending “polar catastrophe” (and no reason for one, since the surface (metal) layer is already metallic. This work has been submitted for publication. We (PI and collaborator R. Pentcheva and students) have also provided an invited overview paper on theoretical work on polar oxide nanostructures and comparison to experimental findings.

Half-metallic behavior in transition metal oxides. Our earlier work on possibilities of half metallic ferromagnetism (including those with no net moment, so-called half-metallic ferromagnets) led us to pursue one of our earlier compounds of interest: La_2VCuO_6. We found, rather surprisingly considering the “conventional wisdom” in the field, that the nonmagnetic V^{5+} (d0), Cu + (d10) closed shell, band insulator result is a serious competitor as the ground state of this double perovskite compound. [Pardo & Pickett, *Physical Review* B (2011)]

Density Functional Calculations of Transport Through Single Molecules

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Creating single-molecule transistor technology is a major thrust of the National Nanoinitiative; and experiments to build, measure, and control the current-voltage characteristics of such devices continue, enhanced by interest in novel materials such as graphene.

These efforts vitally need guidance from calculations because of the complexity of modern materials and the vast number of materials and geometries now accesible. This proposal is aimed at developing the theory and methods needed to make such calculations feasible, accurate, and reliable.

Burke is a leading expert in developing density functional theory and approximations used in such calculations. Car has made seminal contributions to the simulation of matter using density functional methods. Together, with prior DOE support, they have already made major contributions in this area, both in finding and understanding the limits of present methods and developing totally new approaches.

The present funding period is focused on building on their previous work, leading to methodologies that overcome some of the existing inaccuracies, and that can then be made available to all workers in the field. There is also a broadening to cover several other deeper and more general issues relevant to these and other calculations. The collaboration will be cemented by travel of junior personnel working with both groups.

Electron Probes of Nanoscale and Subnanoscale Structures and their Dynamics

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The project is a theoretical effort devoted to developing and implementing the theories of the spin dynamics of magnetic moment bearing sub nanoscale entities, such as ultrathin ferromagnetic films, adatoms adsorbed on metallic surfaces, and small clusters of moment bearing adatoms. The theories are basically ab initio in nature. We begin with a description of the one electron structure of the system of interest either within the empirical tight binding approach or, more recently, by a methodology developed for directly incorporating the Kohn Sham dynamic susceptibility generated through application of the KKR method of describing the electronic structure of the system. A many body formalism takes us from the description of the electronic structure at the one electron level through to spin dynamics. We are in active collaboration with several experimental groups. These being the Wiesendanger group in Hambrug, Germany, the group of J. Kirschner at the Max Planck Institut in Halle, Germany, and more recently with Dr. Harald Ibach in Julich, Germany. A central element of our program is the active interaction between our theory and experimental studies of spin dynamics of subnanoscale metallic structures. Of interest are spin waves explored through spin polarized electron energy loss spectroscopy, and also the spin dynamics of single atoms and small atom clusters studied via spectroscopy based on use of the scanning tunneling microscope.

First Principles Exploration for the Origin of Ferromagnetism in Diluted Magnetic Semiconductors

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Rational design and synthesis of novel nanostructures rely on clear understandings of their structural, electronic and magnetic properties in different environments. We propose to develop and apply density functional approaches to address fundamental issues in nanomagnetism, spintronics and molecular spintronics. Explicitly, we will study (1) magnetic anisotropy and spin dynamics in small structures, (2) adatom induced spin-orbit coupling and quantum spin Hall effect in graphene, and (3) magnetic impurities in amorphous Si and Ge semiconductors and alloys. Our research will be performed synergistically with experimental groups nationwide, in particular with Professor W. Ho, a leader who synthesizes, characterizes and manipulates broad range molecular structures with homemade scanning tunneling microscope (STM) apparatuses at UC Irvine. Our theoretical studies will include calculations of many physical quantities amenable for direct comparison with experiments such as STM images, scanning tunneling spectroscopy (STS) including many-body and tip effects, inelastic electron tunneling spectra from vibrations and spin excitations, spectra of x-ray adsorption and x-ray magnetic circular dichroism. The uniqueness of our project is the determination of magnetic anisotropy energies of large systems, which is essential for the understanding of spin dynamics of nano- and subnano-entities. It is our goal to conduct coordinated and creative research on magnetic nanostructures of fundamental importance, with an eye towards finding new materials and phenomena for technological breakthroughs.

We use the pseudopotential plane wave based Vienna ab-initio simulation package (VASP) and our own full potential linearized augmented plane wave (FLAPW) code. While most calculations will be done at the level of local density approximation (LDA) and generalized gradient approximation (GGA), we will use more advanced functionals such as van der Waals non-local potentials and hybrid functionals for better description of structural and electronic properties. We will continuously develop new algorithms and codes to establish functionalities for studies of new science and to achieve excellent performance on the next generation computing platforms.

Spin-Mediated Energy Transport and Dynamics in Quantum Magnets

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The focus of this study is on the 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 onto their fundamental properties and lead to new applications.

Theoretical understanding is being developed for the energy transport phenomena and dynamical properties of quantum magnets in general and, specifically, of the BEC-like, low-D, 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.

Density Functional Theory for Phase-Ordering Transactions

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During FY2011 we made significant progress in two research fronts. One is the development of a self-consistent theoretical procedure to predict the dynamic properties of non-equilibrium colloidal systems. Unlike alternative methods in the literature, the self-consistent procedure completely decouples dynamic variables from thermodynamic functions that are suitable for equilibrium systems. We demonstrated that the dynamic equations are in parallel to and fully consistent with the statistical description of equilibrium systems. With certain assumptions, the self-consistent procedure can be reduced to various conventional theories of non-equilibrium processes. The other major accomplishment is the development of a molecular density functional theory (MDFT) that can be used an alternative to thermodynamic integration methods in molecular simulation of free energies. We have tested the numerical performance of MDFT with the solvation free energies of a wide variety of chemicals including ions and amino acid residues. The new computational procedure is fully compatible with conventional force fields and can be easily integrated with standard simulation packages.

We have also made progress in the application of classical DFT to supercapacitors of ionic liquids and to drying/wetting transitions. We demonstrated that DFT is able to reproduce the transition in the differential capacitance curve from the “camel” shape to the “bell” shape when the ionic density increases. By considering the molecular size, topology, and electrostatic correlations, we examined major factors responsible for the unique features of electric-double layers of ionic-liquids including formation of long-range and alternating structures of cations and anions at charged surfaces. We discovered that the capacitance of an ionic-liquid electrolyte inside a nanopore oscillates with a decaying envelope as the pore size increases.

Time-Dependent Current Density-Functional Theory of Charge, Energy and Spin Transport in Nanoscale Conductors

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The last decade has witnessed an explosion of interest in the theoretical and experimental studies of transport properties of conductors with nanoscale dimensions. On one hand, this interest is motivated by the obvious thrust of creating novel electronics capable of outperforming the present silicon-based technology. On the other hand, novel effects and phenomena arise when electrons are confined to move in regions of space that comprise a relatively small number of atoms. Despite considerable progress in the fabrication and characterization of nanostructures, understanding transport at these length scales represents a challenging problem, as the full many-body problem needs to be solved under the non-equilibrium conditions dictated by the external source that maintains current flow. Here we propose to 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. Our goal is to understand the dynamics of charge, spin and energy in nano-structures 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. 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; and (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 an external environment. The projects proposed are the first of their kind, and may have a large impact on the field of electronic transport, by introducing new ways to think about these problems and to calculate their solutions.

Computational Studies of Hydrogen Interfaces with Storage Materials

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Building on our accumulated knowledge of hydrogen interactions with semiconductors and insulators we have been conducting computational studies with the goal of developing new insights for hydrogen interactions with hydrogen storage materials. Using state-of-the-art density functional calculations, our research addresses the energetics and electronic structure of hydrogen atoms interacting with potential storage materials. In contrast to previous computational studies of bulk quantities, our investigations explicitly address the behavior and interactions of individual hydrogen atoms with the host material. The results provide direct insight into the processes of hydrogen uptake and release, and help in developing guidelines for designing storage media with improved storage capacity and kinetics.

Our studies focus on two classes of materials: metal hydrides and complex hydrides.

- For hydrogen in metals, we are investigating how the electronic structure of hydrogen within the host metal affects its energetics and diffusion behavior. Our studies of hydrogen-vacancy interactions in Al and Mg have revealed interesting differences, for instance in the tendency to cause superabundant vacancy formation, or the effect of vacancies on hydrogen diffusion rates. These results may also have interesting consequences for the understanding of embrittlement.
- Metal hydrides can store large amounts of hydrogen, but due to the high atomic mass of the host element(s) the weight-percent efficiency is typically low. The storage efficiency of MgH_2 is quite good, but the kinetics are too slow. We have performed comprehensive studies of point defects and diffusion in MgH_2, enabling us to identify the dominant diffusion mechanisms. We are extending

these studies to other hydrides, including AlH_3, for which we are al-so performing Kinetic Monte Carlo simulations of the dehydrogenation process.

- For complex hydrides, a major result of our studies is that the point defects that are relevant for transport are all charged. Their formation energy (and hence the kinetics of diffusion and decomposition) thus depends on the electron chemical potential, which in turn is affected by the presence of additives. This explains, for instance, the effect of transition metal impurities on the kinetics of $NaAlH_4$ and related materials. We are also studying $LiBH_4$, $LiAlH_4$, and Li_2NH/$LiNH_2$. For the latter, we have been able to explain the particle-size dependence of the activation energy for decomposition.

Our overall goal is twofold: (1) develop guidelines for designing storage media with improved storage capacity and kinetics; and (2) generate new fundamental knowledge, for instance, about mechanisms that govern ionic transport in insulators.

Resolving Frustration in Complex Materials

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The aim of this project is to develop the theory of novel quantum magnetic materials, in which strong quantum effects, frustration, and spin-orbit coupling play significant roles. Such materials form a relatively unexplored class of compounds, and exhibit properties not found elsewhere. The major results of the project from the past year are summarized below:

We found a global phase diagram for strongly spin-orbit coupled materials close to the Mott metal-insulator transition. Specifically for iridium pyrochlores we predicted the existence of a possible topological Mott insulator state.

We developed a microscopic theory for ordered double perovskite magnets with 4d and 5d transition metal ions. Here strong spin-orbit effects lead to enormous multipolar interactions. This induces several unusual magnetic states such as quadrupolar and octopolar ordered states, as well as a possible quantum spin liquid state.

We showed that some rare earth pyrochlores are described as types of "quantum spin ice.” From an accurate microscopic model, we modeled the magnetic excitations of these materials, and in particular achieved a remarkable fit to data on $Yb_2Ti_2O_7$, in collaboration with the neutron scattering group of B. Gaulin at McMaster university. We also showed that the model Hamiltonian supports a quantum spin liquid state.

Theoretical Studies in Very Strongly Correlated Matter

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During the period of reporting (September 2010- September 2011) the PI has worked with his two graduate students (Edward Perepelitsky and Daniel Hansen), a post doctoral fellow Dr Arti Garg, Professor Gey-Hong Gweon at UCSC. He has collaborated with Prof P. Phillips at UIUC, as well as Professor A. M. S. Tremblay in Sherbrooke (Canada) on various projects. These have resulted in several publications described briefly next. A study of the low density limit of Hubbard model, with a large interaction to bandwidth ratio U/W leads to a clear picture of the formation of the lower and upper Hubbard sub bands, within a Fermi liquid framework. A model study of thermopower in a solvable model in 1-dimension gives insight into the effects of a quantum critical point on this important variable. The Kelvin formula for thermopower, formulated by the PI earlier and the high frequency formula are benchmarked in the 3-dimensional FCC lattice Hubbard model using a version of the dynamical mean field theory.

The PI has proposed a new formalism for the case of extremely large correlations, where the Feynman diagrammatic schemes fail. This leads to a hierarchy of equations in a particle density type variable. The lowest order theory is solved analytically using some simplifying assumptions, and leads to explicit and useful results for the spectral function. This spectral function was tested against ARPES data from various published data sets using both laser and synchrotron light sources. It gives a close agreement for the line shapes. These applications and the formalism are published in two consecutive *Physical Review Letters*. Several predictions concerning the asymmetry of the line shapes follow from the theory that can be tested by high resolution ARPES and also tunneling, and are contained in a preprint.

Theoretical and Computational Studies of Characteristics of Metallic Nanoalloys

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In this renewal proposal we propose to continue the development of a framework for understanding and hence controlling the properties of bimetallic nanoparticles as a function of their elemental composition and size, using as accurate a technique as feasible. While several novel chemical, magnetic, electronic, optical and dynamical properties of alloy nanoparticles in supported or gaseous form are already known, the technological application of these important materials is hampered by the empirical approach of trial and error. Computer modeling of nanoalloy properties has also been the subject of several studies but a systematic knowledge (hence, control) of the structure-property relationships is either incomplete or lacking altogether. A central element of this proposal is to integrate existing models in a coherent methodology, to examine a range of properties of these novel materials so as to have on hand a multifaceted computational tool not only for fundamental research, but also for computer-assisted material design.

The proposed research involves the following stages: (1) determination of stable geometric structures of nanoparticles using many body interaction potentials together with genetic algorithm and conformational space annealing based search schemes; (2) application of first principles electronic structure calculations based on the density functional theory (DFT) for further geometric optimization and determination of bond-length/bond-order hierarchies, etc.; (3) determination of vibrational dynamics (through perturbative DFT and/or lattice dynamics based on model potential) and relative stability of nanoalloys; (4) determination of optical properties of selected nanoalloys using refined version of time dependent DFT suitable for systems with strong electron correlations; (5) determination of magnetic properties of relevant nanoalloys using DFT + dynamical mean field theory; and (6) determination of atomic and vacancy diffusion and structural evolution of nanoparticles using standard kinetic Monte Carlo or self learning KMC. The specific systems will be nanoalloys of Au with Fe, Co and Pd and core-shell alloys of Pt and Ru. The work will be done in discussions with experimentalist in the area with whom the PI has on-going interactions. For stage 1, discussions and exchange of technical information is already established with Ferrando's group in Genova, Italy.

The intellectual merit of this project concerns the development and application of a number of cutting edge, accurate calculational schemes to determine and understand some very promising optical, magnetic, structural (geometry and electronic), and vibrational properties of the proposed bimetallic nanoalloys. In addition, the proposed integrated method would allow the examination of physical and electronic structural properties not readily accessible to experiments. Successful completion of the project will pave the way for tailoring properties of these novel materials for a wide range of applications. Tuning of optical properties of nanoalloys may provide unique identifiers for controlled materials. When used as taggants it would give the material a unique optical signature depending on nanocluster size, composition and shape. The unique magnetic response of superparamagnetic clusters could be used in anti-counterfeiting or tracing controlled materials from production to final utilization. Applications are also targeted for quantum computers, data storage devices, optoelectronic devices, drug delivery, and chemical sensors to name some. Cost-effective applications, however, can only come about through a systematic understanding of the relationship between nanoalloy structure and functionality, as proposed.

Studies of the Marginally Jammed Solid

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A collection of idealized spheres jam into a disordered solid when compressed at zero temperature. Our work has shown that this jamming transition is singular, in that the number of inter-particle contacts at the transition is exactly the minimum number needed for mechanical stability. In the manner of an ordinary critical point, this singularity controls the harmonic as well as the anharmonic properties of the solid in the vicinity of the transition. Our objective is to address the following questions:

(1) How does the system behave when pushed beyond the harmonic regime so that anharmonic effects become important? Our results have shown that the most anharmonic vibrational normal modes exist 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. What is the nature of the energy-barrier distribution? At the jamming transition, anharmonic effects diverge. How do they evolve as the system is compressed above that transition? How are states that are connected by low energy barriers related to each other?

(2) What is the effect of shear stress on idealized sphere packings? How does one localized rearrangement trigger another to lead to macroscopic failure in the form of a shear band? Can we predict from the harmonic spectrum or the anharmonic response how close a system is to the edge of failure?

(3) What is the effect of temperature? Could the anharmonic quasi-localized modes herald the existence of two-level systems or dynamical heterogeneities? Can the normal modes themselves be enough to produce some of the characteristic properties of low-temperature glasses such as the appearance of phonon echoes? How is the jamming transition related to the glass transition?

(4) 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?

We are performing computer simulations of particles with finite-ranged repulsive interactions at the threshold to jamming. We will also use a variety of other potentials that include long-ranged attractions as well as bond-bending interactions. Equilibrium and nonequilibrium molecular dynamics simulations, Monte Carlo simulations and numerical minimization techniques will be employed.

We have been able to generalize many of the results for idealized spheres to more realistic systems. Several laboratories, including our own, are providing experimental tests to these ideas. We expect that the studies outlined in this proposal will not only provide theoretical insight to general packing problems, but also reveal the underlying cause of some of the longstanding experimental phenomena found in disordered solids.

Quantum Mechanical Simulations of Complex Nanostructures for Photovoltaic Applications

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Funding:	$150,000

This project started on August 15, 2011, with the primary objective of developing new first-principle approaches for electronic excitation calculations that are more accurate than traditional density functional theory (DFT) and are applicable to systems larger than what current beyond-DFT methods can treat. The PI hired a postdoctoral fellow mainly working on this project, who arrived on October 15. Currently the postdoctoral fellow is learning the basic concepts and fundamental physics involved in electronic excitations, and the existing computational methods based on the many-body perturbation theory (MBPT) with Green functions, namely the GW/BSE scheme. He has carried out calculations of quasi-particle energy levels and optical absorption spectra for bulk semiconductors, organic molecules, and Si quantum dots (QDs), comparing various approximations and models used in GW/BSE. The PI also has two graduate students performing research projects along this direction. William is PI's MS student, who studies electronic band structures of graphene nanomeshes (GNMs) with complex structures, in order to shed light on GNMs' band gap opening mechanism and to evaluate band gap as functions of a variety of structural parameters. Marc is PI's PhD student, who investigates the origin of the variation of exciton binding energy in semiconductors. His preliminary results clearly show that exciton binding energy decreases as the spread of electron distribution, which measures the magnitude of electron delocalization, increases. This is due to the increased electronic screening when electrons tend to be more delocalized. Furthermore, the spread distribution of the top valence electrons is of central importance in determining excitonic screening, which leads to weakly bound electrons and holes in semiconductors. Thus, the variation of exciton binding energy in semiconductors can be understood from the computed magnitude of electron delocalization of top valence bands of these materials using DFT.

CMCSN

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Funding:	$320,000

In this multi-investigator collaborative project, scientists including Garnet Chan (Chemistry, Cornell), 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. Strong correlation effects are basic to many areas of condensed matter physics, materials science and chemistry. They arise when the energy scale of the electron-electron interaction is as important as the energy scale associated with the formation of chemical bonds or electronic energy bands. Strong correlation effects cause the unique superconductive, magnetic and metal-insulator transition properties of transition metal oxide and pnictide materials, control the magnetic and electron transport characteristics of molecular complexes involving transition metal ions, and become important as chemical bonds are broken.

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 will take the next step forward by linking the different fields. Faculty members in the network will jointly mentor postdoctoral researchers and graduate students working to bridge the different fields. The network will also support frequent and extended visits from one institution to the other, enabling the cross-fertilization between different approaches which is essential for the progress of science.

The network scientists will work together to build on the successful use in chemistry of modern wave function based techniques such as density matrix renormalization group and Jastrow projected BCS wave functions to devise new methods for computing the energetics and dynamics of realistic Hamiltonians describing bulk correlated electron materials and to apply the Green's function based dynamical mean-field techniques recently developed in the physics context to treat strongly correlated problems of quantum chemistry. The network will also investigate the utility of quantum-chemical wave-function-based techniques as "solvers" for the equations of dynamical mean field theory. The insights gained from applying methods outside of their original domain will also be used to improve the methods within their original domain of application. The expected outcome is a suite of new methods for tackling the heretofore challenging strong correlation physics of molecules and solids, which will lead to new insights into basic condensed matter physics, materials science and chemistry and to new capabilities for modeling novel materials which may form the basis new classes of devices for sensing, energy harvesting and storage, and computing. The new ideas, algorithms and computer codes will be made available to the community via the scientific literature, presentations and focus sessions organized at conferences and, if appropriate, via distribution of open-source software or contributions to existing quantum chemical packages.

Theory of Surface and Interface Physics of Correlated Electron Materials

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Funding:	$150,000

Correlated electron' materials have remarkable and potentially important electronic properties including very high transition temperature magnetism and superconductivity and highly enhanced optical and magnetic responses. These properties arise from the strong quantum mechanical interactions of electrons in solids, and their understanding and control is one of the grand scientific challenges of our era. Correlated electron materials may be the basis of new technologies which will help meet the nation's energy and technology needs, but if this potential is to be realized we must understand how to fabricate them as devices. This means that it is essential to understand both the changes in correlated electron behavior that occur at the surfaces and interfaces essential to any working device and the new effects that may be obtained in precisely designed materials.

The research proposed here is theoretical and computational; it aims to develop the concepts and techniques needed for this new field of science and to apply the results to determine how appropriately engineered nanostructures can be used to obtain novel properties not found in bulk materials and to optimize properties already known. The benefits will include advances in the understanding of the basic physics of correlated electron materials and new results and methodologies enabling the rational design of materials with desirable electronic properties.

Band-theoretic methods will be used to establish basic energy scales and material-specific parameters. More sophisticated many-body techniques, including dynamical mean field theory, will then be used to determine the correlated electron physics including charge distribution, optical and raman response, magnetic phase diagram, as well as to examine the possibility of new excitonic states and new modalities for transitor effects. We will work closely with experimental groups to develop the theoretical modeling tools and phenomenological understanding needed for the interpretation of the spectroscopies which are essential for resolving the basic physics of the materials. The theory will also be used to predict material configurations which will optimize desirable electronic properties such as metallic ferromagnetism with a high spin polarization and transition temperature. The investigation will center on transition-metal-oxide based materials with multiply-occupied d-shells (V, Fe, Cr, Co and Ni), which our previous theoretical work suggests are the most likely candidates. We will also engage in two high-risk/high reward projects: investigation of the possibility of creating new kinds of electron-hole liquids in nanostructures based on Mott and charge-transfer insulators with small and tunable gaps, and studies of the dynamics of the gate-voltage-switched Mott transition. If successful the results would enable the creation of new quantum states of matter and provide insights into nonequilibrium quantum field theory and new routes to ultrafast, low power electronics.

Bridging the Quantum-Chemistry Solid-State Divide: Theory and Application to Molecular Crystals

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Funding: $285,000

TENSOR NETWORKS AND LOCAL CORRELATION

We have implemented our proposed tensor network approach for local correlation for two ab initio theories: second order Moller-Plesset theory (MP2) and coupled cluster singles and doubles theory (CCSD). Our implementation is now at a sophisticated production level and includes both the use of density fitting approximations, as well as F12 corrections for explicit correlation. We have benchmarked our implementation against the state of the art Pulay-Saebo local correlation implementations of Werner and Schuetz. Our results are highly encouraging. Our implementation is both significantly faster (by an order of magnitude), uses less memory (by an order of magnitude), and achieves greater accuracy (in practical calculations) than the best Pulay-Saebo implementation. Our methods will soon be available for use by the general community as the default local correlation method within the Molpro package. Two manuscripts will be submitted shortly.

GOING BEYOND LDA+DMFT AND QUANTUM CHEMISTRY

We have developed a quantum chemical version of ab-initio dynamical mean-field theory that does not rely on the LDA+DMFT approximation, thus avoiding the troublesome double counting approximations. The starting point is a crystalline Hartree-Fock calculation which allows an exact counting of the Coulomb interactions. To our knowledge, this is the first realistic DMFT application which does not suffer from the double counting approximation. This work has been published in the *Journal of Chemical Physics*, and was selected as a highlight article by the editors.

We are currently working on improved solvers for DMFT inspired by quantum chemical wavefunction correlation methods, and looking at their application to surface chemistry problems.

EXCITED STATES IN THE PRESENCE OF A DIELECTRIC ENVIRONMENT

We have made significant advances in coupling first-principles ab initio excited-state calculations to coarse-grained descriptions of a dielectric environment. This work has resulted in a submission to *Physical Review B* (preprint available on arXiv:1104.3175) in March/April of 2011, currently under review. The submitted work deals with a rigorous formulation of what we call a joint time-dependent density functional theory, which extends our work on equilibrium joint density-functional theories to the time-dependent case. The new theory allows a rigorous treatment of the environment in time-dependent density functional theory calculations of excited states, which we have demonstrated successfully with a number of calculations showing favorable agreement with experimental solvatochromic shifts.

We have since considered similar treatments of the environment in the full GW and Bethe-Salpeter equation (BSE) contexts and have made significant progress on those fronts as well, presenting them at the 2011 American Physical Society (APS) Annual March Meeting. Our work is now focusing on improving the cancellation of errors between the vacuum and solvated calculations to obtain quantitative solvatochromic shifts.

Quantum Chemistry via Walks in Determinant Space

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Students:	1 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding:	$282,996

There are many chemical questions of practical interest to DOE that could be answered if there were an electronic structure method that provided consistently accurate results for all systems at an affordable computational cost. The coupled cluster method with single, double and perturbative triple excitations (CCSD(T)) is the most frequently used high-order method, but it has known deficiencies, e.g., in the description of stretched bonds. The full configuration interaction (FCI) method is the most robust method for treating electronic correlations, but it is little used because its computational cost scales exponentially in the size of the system. The largest calculation to date employed 10^{10} determinants. In this regard, there has very recently been a breakthrough. The Alavi group at Cambridge University has developed a stochastic approach to FCI -- combining it with ideas from quantum Monte Carlo (QMC) -- called FCI-QMC that allows one to go well beyond this number. The computational cost is still exponential in the system and basis size but with a much reduced exponent. If one is willing to settle for an approximate (but still accurate) FCI energy they have demonstrated that it is possible to have as many as 10^{110} determinants in the FCI space. While this is a breakthrough in the number of determinants, it is a relatively modest increase in the size of the system and the single-particle basis that can be used because of the exponential scaling, so further improvements are needed to extend its range of applicability. QMC methods suffer the notorious sign problem. Typical QMC calculations in electronic structure use a constraining condition to control the sign problem, achieving low-polynomial scaling but sacrificing exactness. FCI-QMC takes advantage of random walks in the space of determinants, where the sign problem is less severe, and uses cancellation of random walkers in a discrete determinant space to realize an algorithm which is in principle exact.

The purpose of this CRT is to seize the opportunity that the advent of FCI-QMC presents to develop further improvements to the method to incorporate into FCI-QMC as many of the desirable features of existing QMC methods as possible, e.g., a very weak dependence on basis size in the diffusion Monte Carlo (DMC) method, techniques from auxiliary-field QMC (AFQMC) which also uses a random walk in Slater determinant space, and to apply the method to systems of relevance to the alternative energy industry -- hydrogen storage systems, energetic molecules and the dissociation of CO_2. To do this we have assembled a small interdisciplinary team of researchers who have played a leading role in developing quantum chemistry methods, QMC methods and density functional theory methods. Accordingly this effort is supported by both computational chemistry and theoretical condensed matter physics. It is our hope that with the implementation of the proposed improvements, the FCI-QMC method will become a standard method in the toolbox of quantum chemists and physicists interested in high accuracy calculations.

Quasi-crystals and Quasi-equivalence: Symmetries and Energies in Alloys and Biological Materials

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Funding:	$125,000

This grant addresses both the theory of quasicrystal alloy structures as well as biological physics modeling from the standpoint of symmetries and material properties, specifically the origin of left-right asymmetry in organisms. In quasicrystals, we continue to develop methods to determine the exact atomic structure of a complex metallic alloy (out of a family of closely related structures) using pair potentials fitted to ab-initio databases. These are combined with an intelligent form of brute force quenching and/or the use of "tile decoration models," in which the quasicrystal is represented as a space-filling tiling using 2 to 4 types of polygons/polyhedra, with each type having an invariant atom placement like the unit cell of a crystal. Our specific projects cover decagonal Al-Co-Ni, decagonal Mg-Zn-Y, and Zn-Sc-Cu (quasicrystal related cubic phase) A second group of projects involves two different classes of materials which have small, asymmetric clusters inside large icosahedral cages; the task is to predict the shape of the small cluster, its preferred orientation in the cage, and the orientation interactions of neighboring clusters. Our specific projects involve cubic crystals related to quasicrystals: one class is tetrahedra in Zn-Sc-Cu, Zn-Sc, and Ca-Cd; the other class is Al9 or Al10 clusters in Al-Ir and Al-Pd-Mn.

In biology, we are simulating the statistical mechanics of two-dimensional layers of cytoskeletal fibers in the cell membrane, to see how chirality emerges in their coarse-grained properties: microtubule arrays in plant cells, and the actin-myosin layer in animal cells (particularly approaching division). In addition, we do theory support for experiments in the mechanical properties of plant root growth, and in the propagation of the left-right signal by signal diffusion and regulation in the zebrafish embryo.

Quantum Phases of Nanowires: Quantum Monte Carlo Approaches

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Funding:	$90,000

The general goal of this project is to study different quantum phases of one-dimensional electronic systems. We made progress on three topics:

(1) Strongly Inhomogeneous Low-Density Electron Gas: Correlation, Zigzag, and Conductance— While the 1D electron gas is well understood in its simplest context, major issues remain in slightly more complex structures. We are using quantum Monte Carlo (QMC) techniques to investigate in an unbiased way, first, the properties of the liquid/crystal interface in a strongly inhomogeneous system and, second, the linear-to-zigzag transition in a quasi-1D wire. The low-density electron gas, where the Coulomb interaction is large compared to the kinetic energy, is perhaps the simplest strongly correlated system. Progress to date on this part of the project has been mainly technical, namely in developing the computational software needed (in collaboration with C. Umrigar, Cornell). We made substantial progress in this regard; the suite of programs needed for the topics of interest is complete.

(2) From Weak- to Strong-Coupling Mesoscopic Fermi Liquids— The Fermi liquid is a ubiquitous state of electronic matter. Indeed, it is so common that systems can have several different Fermi liquid phases in different parameter regimes (controlled by different fixed points), leading to cross-overs between Fermi liquids with different characteristics. In such a situation, it is interesting to ask how the quasi-particles in one Fermi liquid are related to those in the other. The particular system studied is an Anderson impurity coupled to a finite mesoscopic reservoir described by random matrix theory, a structure which can be realized using quantum dots and wires. We use the slave boson mean field approach to connect the levels of the uncoupled system to those of the strong coupling Nozieres Fermi liquid. This project is nearing completion. We find strong but not complete correlation between the mesoscopic properties in the two limits and several universal features.

(3) Quantum Phase Transitions Caused by Dissipation in Nanowires and Quantum Dots— This new topic was suddenly added to the project last fall because of rapid and fascinating developments in the lab of my experimental colleague here at Duke, Gleb Finkelstein. They investigate tunneling through a resonant level formed in a carbon nanotube quantum dot contacted by resistive metal wires. These contacts create a dissipative environment for the electrons tunneling across the nanotube, thus suppressing the tunneling rate. They find that the shape of the resonant peak crucially depends on the ratio of the tunneling rates from the resonant level to the two contacts. We studied this system theoretically and have shown that it maps onto the problem of a resonant level in an interacting one-dimensional wire; the coupling to dissipation generates an effective interaction in the leads. Through this mapping we are able to extract many of the features seen experimentally and show that the change in behavior from symmetric to asymmetric coupling to the leads is a boundary quantum phase transition.

Correlated Electrons in Reduced Dimensions

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Funding:	$70,000

The study of the quantum Hall effect – a phenomenon which occurs when a two-dimensional electron gas (2DEG) is placed in a strong magnetic field and cooled to ultra low temperatures – continues to provide fundamental insights into the remarkable variety of order possible in strongly correlated quantum systems. For example, the fractional quantum Hall state observed at Landau level filling fraction 5/2 is conjectured to possess so-called "non-Abelian" order. In states with such order, quasiparticle excitations are characterized by quantum numbers similar to ordinary spin quantum numbers but which, unlike ordinary spin, cannot be distinguished by local measurements. The Hilbert space describing such quasiparticles has a built in resistance to decoherence, and for this reason, non-Abelian states have been proposed as possible physical media for realizing an intrinsically fault-tolerant form of quantum computation (so-called topological quantum computation) which would be carried out by "braiding" the world-lines of quasiparticles in 2+1 dimensional space-time.

Another quantum Hall system of current interest is the bilayer system with total filling fraction 1 consisting of two parallel 2DEGs each with filling fraction 1/2. This system exhibits a still poorly understood transition from an incompressible quantum Hall state for small layer spacing to a compressible Fermi liquid of "composite fermions" (electrons bound to two flux quanta) for large layer spacing. The work funded by this award includes the theoretical study of non-Abelian states such as the 5/2 state, addressing in particular how precisely one would use such states to carry out topological quantum computation, as well as the possible phases associated with both regular and disordered arrays of "interacting" non-Abelian quasiparticles. In addition, the effects of the strong "Chern-Simons" gauge fluctuations associated with the composite fermion description of the filling fraction 1 bilayer state (valid for large layer spacing) on the possible instabilities of that state as the layer spacing is decreased are being studied. Finally, theoretical techniques developed by the PI and collaborators in the study of braiding non-Abelian quasiparticles are being applied to the problem of finding new classes of pulse sequences for exchange-based quantum computation using spin-1/2 particles (e.g., electron spins in quantum dots).

Strongly Correlated Electrons

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Funding:	$55,000

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. Collaborations with experimental groups are expected to continue.

A Computational Approach to Complex Junctions and Interfaces

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Funding:	$220,000

This project aims at understanding 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, and van der Waals corrections etc. will be used to calculate physical and chemical quantities needed for addressing problems and issues.

We study problems in a number of complex interfaces and junctions including (a) electron transport through metal-azobenzene-molecule-metal junctions, where the molecule can transform between trans and cis configurations in response to light excitation; (b) bonding, atom diffusion, and magnetization in systems containing the tris(8-hydroxyquinolino) aluminum (Alq3) molecule between two magnetic leads, for its role as insulator spacer in magnetic tunneling junctions; (c) electron dynamics coupled with structural relaxation and phonon-electron interaction after photo-excitation in carbon nanotubes and graphene that are functionalized by adsorbed organic molecule, because understanding such processes may provide hints of mechanisms for photon-electron current conversion; and finally (d) interfacial electronic and magnetic properties, and Schottky barriers of graphite-silicon interfaces and junctions, and Fe-doped amorphous carbon-silicon interfaces. One common theme unifying these systems is that interfacial structure has critical effects on properties, and our investigations based on first-principles can provide guidance, not only interpretation, for experiments on these seemingly vastly different systems.

We also include a major effort to develop a new method and algorithms. Based on the scattering theory, our method combines layer approach and planewave basis in conjunction with pseudo-potentials. The method is optimal for studying electron transport cross molecular- and nano-junctions because the dependence of computational cost on the thickness is a linear function. The new code will be developed and distributed via gnu public license.

Theory Of Novel Superconductors

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Funding:	$105,000

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 two classes of novel superconductors work. The first, 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, one can now try to extract the essential ingredients for the occurrence of high temperature superconductivity. 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.

A second set of systems to be studied are the superconductors formed in 2D systems at the interface between two insulating oxides. While this superconductivity may be of conventional type, there are indications that it is unusually tolerant of magnetism. The project will therefore include studies of exotic pairing of electrons in a 2D gas confined proximate to oxide insulators which support dipolar fluctuations of various types. In particular, prospects for a d-wave pair state from nonlocal excitations will be examined.

TMS: Orbital-Free Quantum Simulation Methods for Application to Warm Dense Matter

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Funding:	$425,000

Warm dense matter is a phrase which physicists use to label condensed matter in a peculiar and highly important regime of temperature and density. The WDM regime is important because it occupies a significant part of the pathway from ambient conditions to inertial confinement fusion and because it occurs also in the interior of giant planets. The regime is peculiar because it is not simply liquid, solid, nor plasma, but has some properties of each. It is therefore a challenging regime to characterize and to control because methods well-adapted to one kind of condensed matter are not well-adapted to another. This challenge is particularly acute for experiment, with the result that there is strong interest in having reliable simulation results.

Much the same challenge, however, applies to simulation. Put simply, what works for classical plasmas omits the quantum mechanics essential to WDM. But what works for ground state solid systems – a set of methods called Kohn-Sham Density Functional Theory (KS-DFT) - does not necessarily include the high-temperature, high-compression physics of WDM. Another challenge is that the KS-DFT methods are drastically more computationally costly than the classical ones. The requirement for large numbers of simulations to probe and interpret experiment makes that cost a crucial barrier to overcome.

KS-DFT makes the contents of the basic DFT theorems workable by introducing a reference independent-particle system (the KS system) with the same density as the physical system of interest. At best, the computational cost of a general solution for the KS-DFT independent-particle states (“orbitals”) goes up as N^3, with N the number of electrons. (Faster, “linear-scaling,” approximations only work for insulators and semi-conductors.) At zero-temperature this is costly but not prohibitive scaling. At the temperatures characteristic of WDM (10,000 to 500,000 Kelvin) it is nearly prohibitive. Some comparatively heroic calculations have been done and continue to be done because the need for the data is so high. But most of those calculations use zero-temperature approximate density functionals as if they were valid at high temperatures.

This project is aimed at both problems. We are developing “orbital-free” functionals for the kinetic energy, entropy, and exchange-correlation contributions to the free energy. To do so, we have been studying the exact properties such functionals must have, testing already-published functionals against one another (to expose systematic differences or similarities), building reference data by developing methods for near-exact treatment of well-defined methods (thermal Hartree-Fock, Path-integral molecular dynamics) on simple system (several Hydrogen atoms in a hard box, finite temperature electron gas) and comparing simulations with existing tools to assess reliability. Several refereed papers have resulted, others are submitted and awaiting review. We have also had several invited talks. See the project web site http://www.qtp.ufl.edu/ofdft for latest information.

K-Edge Resonant Inelastic X-Ray Scattering in Strongly Correlated Materials

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Funding: $156,000

In this project we are focusing on two primary objectives. One is to investigate a dynamical mean-field theory for resonant inelastic x-ray scattering. The other is to develop and solve models for time-resolved probes like time-resolved photoemission spectroscopy or time-resolved x-ray absorption spectroscopy.

There are two subprojects for the RIXS work. One is working out an exact solution within the Falicov-Kimball model for the correlated material, the other is working on the Hubbard model. The first project is having its results written up, where we generically find a two-peak structure to the RIXS in a Mott insulator, one being a dispersive peak whose width changes through the Brillouin zone and one being a less dispersive peak. The Hubbard work requires complex analytic continuation techniques and is still ongoing.

For the time-resolved probes, we are currently working on the response of a Mott insulator to a pumped pulse, which shows how the hot-electron model fails, and we have been looking at the PES for a charge-density-wave insulator, where we find a new paradigm for nonequilibrium phase transitions, where the gap closes while the order parameter is still nonzero, i.e., the field drives the system into a gapless state.

Finally, we are also working on the development of a new numerical renormalization group code for solving impurity models that we call the continuum NRG. It works to restore the continuous nature of the spectral functions by properly coupling them to the delta function state that comes from the traditional NRG via an RPA-like theory. This approach self-consistently determines the broadening of the delta function peaks and should produce more accurate spectra.

First-Principles Investigation of Complex Materials Properties

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Funding: $155,000

This project concentrates on studying complex materials properties using first-principles electronic-structure methods. The computational tools that we will employ include density functional theory (DFT) within the local-density or generalized gradient approximation (LDA or GGA), the pseudopotential method with a plane-wave basis, quantum Monte Carlo methods for systems with considerable electron correlation, density-functional perturbation theory for the vibrational properties, and nonequilibrium Green's function methods for electron transport. Our goal is to unambiguously explain the phenomena observed in the experiment and to reliably predict new materials properties.

In this funding period, we plan to focus on two-dimensional (2D) electronic systems that exhibit interesting physics not present in typical bulk systems. 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 for this system. The high carrier mobility and the ease to create patterned structures have generated a lot of excitement about the possibility of using graphene to build microelectronic devices. We have identified several important research directions to be covered in this funding period. These include: (1) full-scale transport calculations for graphene ribbons with realistic metal leads, which will be carried out with the nonequilibrium Green's function method together with a DFT Hamiltonian; (2) chemical functionalization, which is believed to be one of the promising methods to manipulate the physical and chemical properties of graphene; (3) a quasiparticle state involving enhanced electron-phonon interaction at high magnetic fields in order to explain the unusual Landau level splitting observed in the measurement of the quantized Hall conductivity; and (4) the nature of electron-electron interaction for massless electrons. These projects address different aspects of graphene physics and major application issues related to the electronic properties of this unusual two-dimensional system.

Structure and Dynamics of Material Surfaces, Interphase-Interfaces and Finite Aggregates

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Funding:	$225,000

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 and the guiding directions of this research program. The 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. Main topics of the proposed research and educational program include the following:

Properties and Transport in Inorganic and Organic Nano-Structures: Wires and DNA: first-principles studies of semiconductor nanowires and their contacts to metals, chemical reactions of nanowires and coating of nanowires, charge transport in DNA.

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 qubits in quantum computers, formation of crystallites in cold atom trap, studies of the spectral and transport properties of interacting electrons in graphene quantum dots, with implications pertaining to fractional quantum Hall effect signatures.

Nanoclusters: charged water nano-droplets and artificial photosynthesis: 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, transitions between interior and surface excess electron attachment, and hydrogen generation in doubly charged water nanodroplets.

Nanojets, Virtual Nano-nozzles: Development, with the use of large-scale atomistic simulations, of practical methods for the generation of liquid nanojets, with particular emphasis on the concept of "virtual nozzle," where a nanojet is generated via flow in a heated injector. Simulations of collisions of nanojets with solid surfaces and surface patterning, as well as transfer of bio-materials through lipid bilayer cellular plasma membranes.

Theory of Electron Imaging in 2DEGs

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It is a good bet that information processing technologies of the future will involve electrons and their transport. That is also true today of course, but the electron transport used today is largely classical, i.e., incoherent. Increasingly, quantum coherence will play a role in the devices of the future, as a side effect of size reduction, and as a design goal. We are flying blind to the extent that we do not understand how electrons move about in these devices, how they keep or lose their coherence, and how their spatial and spin degrees of freedom are interrelated and can be beneficially harnessed. This proposal suggests a path to better understanding of two important and large classes of coherent electron devices, namely two degree of freedom electron (and hole) gasses (2DEGS and 2DHGS), and quantum wires. The path is a synergistic one, in collaboration with ongoing experiments in the Westervelt lab at Harvard. While we can point with pride to prior accomplishments, many of the biggest challenges remain, namely precise understanding of the workings of these devices and ways to harness them to good effect. Our group at Harvard has a powerful set of theoretical tools already in place to attack these issues. An example being the Heller group thermal quantum wavepacket codes, which perform thermal averages over conductance in realistic devices with coherent wavepackets, are new, and may one day become more widely available but are now necessarily "proprietary." Classical trajectory (ray dynamics) information is also invaluable as an approximation and guide, as is the semiclassical treatment which springs from it. We have developed such codes, with built in simulations of the effective potentials felt by the electrons in 2DEGS, due to impurities and especially partially screened delta layer donor atom potentials.

Other tools are purely theoretical, such as our understanding of the branched electron flow discovered in ballistic 2DEGS in terms of nonlinear dynamics of phase space flow. In addition, we have codes and theory aimed specifically at the conductance and imaging in quantum wires, in the few electron regime where quantum effects are crucial. The imaging is accomplished with a moveable charged "scanning probe microscope" (SPM) tip, with sub-angstrom resolution. We will model the tip potential, as it interacts with 2DEGS and wires, using SETE, during the entire period of the grant as the need arises. The extraction of the effective potential of individual 2DEG samples from the SPM data may take one or two years to accomplish, first using known electron effective potentials which we can compare with the reconstruction, and then with experimental data. Meanwhile we will bring up work on quantum wires in parallel, beginning with a simulation of electron wave imaging, using the shift in Coulomb blockade peaks with tip position. We suspect that defects and impurities are important, and these will be incorporated next, probably in the second and third years of the grant period. The code, which can now already handle four or five fully correlated and quantum mechanical electrons including conductance, will be improved through the use of new basis set variational techniques to incorporate perhaps twice that number of electrons. Starting in the second year, we will turn to spin sensitive imaging, including the spin-orbit dynamics in our wave packet codes.

Non-Equilibrium Physics at the Nanoscale

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The controlled fabrication of nanoscopic quantum structures has led to the discovery of a plethora of novel quantum phenomena, ranging from the observation of Kondo screening in quantum dots to quantum imaging in quantum corrals. The microscopic origin of these phenomena lies in the interplay between quantum confinement and the resulting discrete eigenstates of the nanostructure, and interaction effects. While the above phenomena arise mainly in equilibrium, the question naturally arises of how this interplay affects the non-equilibrium properties of the nanoscopic structure, and in particular, the charge transport through it.

Using the non-equilibrium Keldysh Greens function formalism, we have shown that quantum confinement in nanoscopic quantum networks leads to the emergence of current eigenmodes which are the non-equilibrium analog of the equilibrium eigenmodes in the density of states. Each current eigenmode exhibits a characteristic spatial current path which is determined by the interplay between the geometry of the quantum network, the degeneracy of the eigenstate associated with the current transport, and the width and location of the leads. This implies that the spatial current paths can be altered by gating the network. In the ballistic (quantum) limit, these current patterns exhibit two distinctive features. First, along certain links in the network, a current flows opposite to the applied bias (the total net current of course flow in the direction of the applied bias). Second, the eigenmodes exhibit closed loops of circulating currents, even in the absence of a magnetic field. The latter can be characterized by the enstrophy, which shows an inverse relation to the magnitude of the net current flowing through the network.

To account for the effects of dephasing on these current modes, and the associated spatial current paths, we have considered the effects of an electron-phonon interaction in the quantum network. We demonstrated that in the high-temperature approximation of the non-equilibrium Dyson equation, the effect of an electron-phonon interaction on the network’s equilibrium electronic structures (as described by the retarded Greens function) and on its non-equilibrium charge transport (as reflected in the Keldysh Greens function) can be self-consistently computed. In particular, we find that with increasing dephasing, the current patterns in the network evolve smoothly from those of the ballistic limit to those of classical resistor network, with backflow and circulating current loops eventually disappearing.

Moreover, we proposed that the spatial current paths inside a quantum network can be experimentally measured using a scanning tunneling microscope. In particular, we showed that by simultaneously measuring the current flowing from the STM tip into the network, and from the network into the attached leads, it is possible to identify the sites of the network with a high current density. Moreover, we demonstrated that this probe can distinguish between the case where the spatial current pattern arises from a single ballistic path, and the case when the current pattern arises from a superposition of ballistic paths. In contrast to previous experimental probes that possess a spatial resolution of 60nm or more, this new technique provides insight into the spatial current patterns with atomic resolution. This new method for current imaging is currently being investigated in collaboration with the experimental STM group by H. Manoharan at Stanford University.

Finally, we demonstrated how the microscopic out-of-equilibrium parameters of the network in the presence of dephasing, such as the local charge density, can be related to the “local electro-chemical potential” obtained via potentiometry.

These results provide important new insight into the question of how the interplay between quantum confinement, interactions, and dephasing give rise to the local charge transport in nanoscopic quantum networks. This in turn will enable us to manipulate non-equilibrium charge transport at the spatial level.

Laser-Induced Ultrafast Magnetization in Ferromagnets

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Funding:	$220,000

The proposed research, on the campus of Indiana State University, will focus on the emerging field of laser-induced femtosecond (fs) magnetization in ferromagnets or femtomagnetism with potential applications in magnetic recording. The goal of this phase of the research is to reveal the mechanism of ultrafast demagnetization; nickel will be used for the example. This research will also focus on training young researchers and students through active research and education. The research team led by Dr. Zhang includes a research assistant and ISU physics undergraduates. We will first compute the laser-induced spin and orbital momenta changes and establish the missing link between spin and orbital dynamics. Then we will compute and compare with experimental signals for two ultrafast x-ray based and element-specific techniques. Two immediate impacts from our research will be that (1) it will reveal how light polarization first affects the orbital momentum and then the spin momentum and (2) it will establish a new speed limit for the future magnetic recording.

Magnetism in Non-Traditional Materials

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Funding: $118,000

We propose to use a ``bottoms-up'' approach to investigate the outstanding issues pertinent to the phenomena of induced magnetism in doped non-traditional inorganic materials (D-NTIMs) using state-of-the-art theoretical methods. We will build on our previous DOE funded work (DE-FG02-00ER45817) on the magnetism of polymeric forms of carbon and extend our investigation into D-NTIMs with a view to provide a unified view of the physical processes responsible for the appearance of magnetism in these two dissimilar classes of materials. Since it is well understood that magnetism is a manifestation of correlation effects, we propose a theoretical investigation of a number of pilot systems at a level beyond DFT/GGA theory, namely the CI, the Coupled-Cluster, the MP_2, the DFT/GGA+U and the Optimized Effective Potential methods. The pilot systems include the doped/defected systems: ZnO,TiO_2, SnO_2, and graphitic systems, all in bulk and nano phases.

Theory of Fluctuations in Superconductors

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Funding: $103,000

This is an overview of the DOE project in progress during FY 2011, "Theory of Fluctuations in Superconductors." Below listed are highlights of two recent researches.

(1) TWO-COMPONENT NATURE OF THE GIANT MAGNETORESISTANCE PEAK IN DISORDERED SUPERCONDUCTING FILMS

Background: A number of disordered superconducting films exhibit very unusual non-monotonous magnetoresistance in the vicinity of the superconductor-to-insulator quantum phase transition. Perhaps, the most dramatic effect occurs in In20x films, where the resistance may change some 6 or more orders of magnitude in the vicinity of the transition as the magnetic field increases. The peak has remained a mystery for more than 30 years since the early work of Hebaard and Paalanen.

Recent Work: One of the recent achievements of the PI is the elucidation of the nature of the giant magnetoresistance peak. The hint came from the experimental work of Sacepe, who recently observed the Efros-Shklovskii-type temperature dependence of the resistance, on the high-field side of the peak. This behavior is a smoking gun of the Coulomb glass phase, which occurs routinely in various strongly-compensated semiconductors, and is described by essentially classical theory of variable-range hopping, where localized carriers hop between metastable minima in the Coulomb potential. By including pairing tendency in the variable-range-hopping theory, the PI has proposed and solved a new two-component

Coulomb glass model and showed that it hosts a giant resistance peak, which occurs due to a competition in transport between electrons and pairs and leads to a bottleneck phenomenon - the peak.

(2) PROPOSED ARPES EXPERIMENT TO DETECT PAIRED ELECTRON POCKET IN THE HOLE-DOPED CUPRATES

Background: The nature of the pseudogap state and pairing in the cuprate superconductors is arguably the most important and controversial problem in condensed matter. The experimental discovery of small pockets in the underdoped cuprates by Taillefer et al. led to a number of new ideas, in particular to a theory by Galitski and Sachdev, which is consistent with a large volume of experimental data. The theory also contains a clear pairing mechanism originating from orientational spin fluctuations in the Neel state. The highlights of the theory are as follows: The Neel order yields a folding of the large hole Fermi surface and an electron pocket near the antinodes. These electrons were shown to be strongly paired due to fluctuations, which may be a simple reason they are not seen in ARPES. However, they contribute to transport along with unpaired nodal holes and lead, in particular, to a change-of-sign in the Hall effect. Strong magnetic fields depair the antinodal electrons and open up their Fermi surface, hence, the oscillations. To confirm or rule out this theory, an experiment is needed to directly visualize the electron pocket. However, ARPES cannot be done in a high magnetic field.

Recent Work: The principal investigator has proposed an experiment that might provide a conclusive resolution to this question. Assuming that there indeed exists a strong pairing in some part of the Fermi surface above Tc, it was proposed to perform ARPES measurement in the presence of high transport currents. The idea is that it would depair the electrons and open up the Fermi surface (just like the magnetic field in the oscillation experiment). This proposed experiment is currently under way in several laboratories and the PI has been communicating directly with experimentalists about it.

Strongly Correlated Electronic Systems: Local Moments and Conduction Electrons

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Funding:	$160,000

In many materials of current interest the repulsion between electrons plays a dominant role. The resulting strong correlation between electrons modifies band theory results and often leads to local moment formation and competition between magnetism, superconductivity and other new states of matter. A pervasive theme in modern condensed matter physics is the contrast between local moment formation and the itinerancy of conduction electrons. As an example, it was discovered several years ago that a conducting layer forms at the interface between two insulating oxides. Recently, superconductivity and ferromagnetism are also found in this structure. We are developing a theory to explain the appearance of ferromagnetism due to the formation of local moments at the interface, and how superconductivity can co-exist with it. Another project is to create an exotic kind of superconductivity in systems with strong spin-orbit coupling and use it as a platform to search for a novel state called the Majorana bound state.

Modeling the Self-Assembly of Ordered Nanoporous Materials

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Funding:	$185,000

This project is about modeling the formation of ordered nanoporous materials using statistical mechanics. In the chemical process industries, porous materials are used as catalysts and catalyst supports, as well as in adsorption and membrane separations processes. In microelectronics porous materials are used, for example, as low-k dielectric materials and optoelectronic devices. Chromatographic separations using porous material are ubiquitous in biotechnology and analytical chemistry. Emerging applications include sensing, tissue engineering and enantioselective separations. An important goal in the materials science research in this area is that of tailoring materials for specific applications. This can be achieved through control of pore structure, size, and shape, as well as the chemistry of the material components. To date, enormous progress has been made; however, this progress has been primarily through trial and error experimentation guided by the intuition of the researchers. Relatively little fundamental understanding of the key molecular scale processes is available. Our project addresses this lack of fundamental understanding through the development and application of nanoscale models of these systems and their computational study via the methods of statistical mechanics.

We focus on two classes of materials: (1) all-silica zeolite framework structures, which are microporous crystalline materials with pore sizes typically less than a nanometer, and (2) ordered mesoporous silicas, in which the order in the system is on the length scale of 5-10 nanometers. The syntheses of these types of materials are representative of a spectrum of ordered nanoporous materials syntheses involving polymerization of silica in the presence of structure directing agents or templates. Under our previous DOE award we developed two models of silica polymerization, both focusing on the assembly of corner-sharing SiO_4 tetrahedra. The present project builds on these accomplishments. During 2011 we have made progress in the following areas: (1) further investigation of the mechanism of silica polymerization in the absence of templates using the models we have developed; (2) introduction of templates into our off-lattice model of silica polymerization; (3) identification of microporous crystalline ground state structures (zeolite analogs) of our lattice model of silica. This is a precursor to modeling the self assembly of such structures in the presence of structure directing agent; and (4) simulation of the assembly of ordered mesoporous silica materials using surfactants as structure directing agents. We now have the capability to model silica polymerization simultaneously with surfactant driven mesophase assembly. This permits us to simulate the assembly of ordered mesoporous silica materials using surfactants as structure directing agents.

Charge Frustration, Spin Singlets and Superconductivity in the 1/4-filled Band Paired-Electron Crystal

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Funding:	$140,000

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 (this feature is apparently not shared by the hole-doped cuprates). In the present theoretical research proposal, we propose investigation of 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 one-quarter, 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.

Charge and Spin Dynamics in Bulk and Heterostructured Dilute Magnetic Semiconductors

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This project is concerned with the carrier dynamics of dilute magnetic semiconductor (DMS) in bulk and heterostructures. DMS have attracted much attention as a promising basis for spintronics devices. An intense experimental effort is underway to study the transport and optical properties of ferromagnetic semiconductors such as (Ga,Mn)As, and many interesting features have emerged: negative magnetoresistance, anomalous Hall effect, non-Drude dynamical conductivity, and resistivity maxima at the Curie temperature. One of the main controversies concerns the nature of the itinerant carriers in DMS: do they reside in the valence band, or do they form a separate impurity band? Available theories based on the valence band picture have led to some inconsistencies with recent experiments, but were not fully conclusive, since a detailed microscopic description of disorder and dynamical many-body effects was lacking.

Building on our results from previous DOE support, we propose to develop a theory of charge and spin dynamics in DMS based on a combination of the memory-function formalism and time-dependent density functional theory (TDDFT). This linear-response based approach will address two important issues: correlated disorder, which requires a treatment beyond the usual relaxation-time approximation, and dynamical many-body effects such as the spin Coulomb drag. We will thus be able to shed new light on nature of the itinerant carriers in DMS and their transport and optical properties. The following two key areas will be investigated:

(1) Transport and optical conductivity in DMS. We will calculate static and dynamical conductivities in (III,Mn)-V bulk systems, with particular emphasis on clustering and magnetic ordering of the Mn impurities, treated beyond the relaxation-time approximation. The host valence band structure will be described using k.p Hamiltonians. Dynamical many-body effects within and beyond the random-phase approximation are accounted for in TDDFT. Realistic impurity correlations, obtained via classical Monte Carlo simulations, will be used as input in the memory-function formalism. The resulting conductivities will be compared with recent infrared spectroscopic data.

(2) Collective excitations in DMS heterostructures. The linewidths of collective charge- and spin-density excitations in semiconductor quantum wells are an alternative probe for disorder and many-body effects. We will focus in particular on intersubband spin plasmons, including spin-orbit coupling and dissipation through the spin Coulomb drag. Disorder scattering will be included with the memory-function formalism. The approach will then be applied to study collective excitations of the carriers in DMS quantum wells, with an emphasis on the change of plasmon properties as the system becomes ferromagnetic. This suggests new types of optical experiments to study the interactions of itinerant carriers and magnetic impurities in DMS.

Fundamental Studies of Complex Oxides and Their Interfaces

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Funding:	$130,000

The project focuses on developing a fundamental understanding of the physics of the correlated-electron oxides and their interfaces using modern computational techniques. The intellectual challenge is to understand the strong interplay between a variety of effects such as the strong correlation, Jahn-Teller effect, orbital ordering, coupling between the spin, charge, and orbital degrees of freedom, and competing magnetic interactions such as the super exchange and double exchange, which results in a rich variety of ill-understood phenomena in these materials. Successful understanding of the behavior of the oxides could lead to potential new devices different from the semiconductor devices. Specific research projects include: (1) characteristics of the two-dimensional electrons at the $LaAlO_3|SrTiO_3$ interface and their possible phases, (2) the Jahn-Teller coupling and origin of the Kondo effect at the interfaces, and (3) Skyrmion state and the Dzyaloshinski-Moriya interaction in bulk magnetic solids. We use the ab initio density-functional methods and appropriate models to describe these phenomena.

Computational methods include density-functional theory (DFT) techniques, viz., the linear muffin-tin orbitals (LMTO) methods to solve the DFT, “constrained" DFT, and the DFT+U equations, as well as the Lanczos exact diagonalization technique for lattice fermions, which is used as a complementary tool to DFT for solving correlated electron problems on finite lattices. The LMTO method is being developed further for treating correlated electron materials.

Time-Dependent Current Density-Functional Theory of Charge, Energy and Spin Transport in Nanoscale Conductors

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Funding: $105,000

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 nano-structures 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, includes 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.

Dynamics of the Magnetic Flux in Superconductors

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Superconductors are at the forefront of condensed matter research due to the deep fundamental physics behind their properties and because of their practical applications. Applications that include the generation of ultrahigh magnetic fields and microwave radiation, and the use of Josephson effect for manufacturing of sensitive magnetic field probes – superconducting quantum interference devices. Future applications of superconductors may include the reduction of energy losses in transmission lines and the implementation of flux and charge qubit, elements of ultrafast quantum computers. Studies of the dynamics of the magnetic flux in superconductors are crucial for making progress in these areas. The work on the DOE grant at Lehman College is advancing the knowledge of physics of superconductors and their potential applications by addressing the fundamental and practical questions of the physics of superconducting materials and circuits.

Recently pursued research topics include the dynamics of the magnetic flux induced by the motion of dislocations in a type-II superconductor subjected to mechanical stress. This effect can be used for developing novel stress tensors based upon superconducting materials. Instanton-glass model of a superconductor-insulator transition in disordered thin films has been studied, following recent experimental work in this area. Classical and quantum effects arising from electromagnetic coupling between a superconducting weak link and a nanomagnet have been investigated, and theory of macroscopic quantum tunneling of the magnetic flux in the intermediate state of a type-I superconductor has been developed.

Current work and research planned at the nearest future include extension of the superinsulator model that takes into account quantized vortices. This would allow comparison of theoretical predictions with experimentally observed dependence of the superinsulator state on the magnetic field. Dynamics of a nanomagnet inside a planar Josephson junction will be studied with an eye on a possible memory unit controlled by voltage. Computation of the tunneling rate for a superconductor - normal metal interface in type-I superconductors will be performed and compared with recent experiments in lead. The Skyrmion-molecule model of electron pairing will be explored in the context of high-temperature superconductivity in oxides and pnictides. The DOE sponsored research at CUNY Lehman College is integrated with education through involvement of graduate and undergraduate students.

Tailoring Magnetism and Spin in Quantum Dots

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Funding:	$140,000

Magnetic doping of semiconductor 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. In contrast to the bulk structures, adding a single carrier in QDs with carrier-mediated magnetism can have important ramifications. An extra carrier can both strongly change the total carrier spin and the temperature of the onset of the magnetization. Magnetic QDs share many similarities with their non-magnetic counterparts and both systems can be viewed as artificial atoms with shell structure and versatile control of number of carriers (by doping, applying gate voltage or illumination).

Unfortunately, even many qualitative features related to magnetism and spin in these systems are still poorly understood. To address this situation we will develop a comprehensive framework suitable to study the interplay of many-body effects and quantum confinement in small magnetic systems with a specific focus on the inclusion of spin fluctuations and developing computational methods beyond the mean-field approximation. We will also explore novel possibilities to control the ordering of magnetic impurities and carrier spin in QDs, even at a fixed number of carriers, as well as to provide proposals for their experimental implementation.

Under this grant we have already published work to explain: (1) experiments demonstrating a robust magnetic ordering in QDs, (2) an unexpected occurrence of closed-shell systems (highlighted in September 2001 MRS Bulletin http://journals.cambridge.org, and 3) versatile gate-control of ferromagnetism in magnetically doped quantum wells. Our preliminary results also reveal a counterintuitive regime of temperature-enhanced magnetism in QDs.

Quantum Theory of Semiconductor Photo-Catalysis and Solar Water Splitting

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Funding:	$140,000

The alloy of ZnO in CuCl is at present one of the most promising materials for solar photocatalysis. We submitted a manuscript in January 2011, which was published in *Physical Review B* in April 2011, containing a careful computational study of this alloy. Extensive total energy calculations by density-functional theory (DFT) give us phenomenological interaction parameters. Monte Carlo calculations then predict a phase diagram. We show that homogeneous alloys can be prepared at T > 900K over the full concentration range. At lower T, phase separation is predicted, with a layer-ordered phase at 50% concentration, and a strongly first-order order/disorder transition at 900K. The equilibrium high T disordered phase is predicted to retain much short-range order. Because the ordering temperature of 900K is relatively low, kinetics will inhibit ordering and homogeneous alloys should be comfortably metastable over the whole range. Unfortunately, the short-range ordering has a consequence that the optical band gap is ~2.5 eV, higher than optimal, and higher than would occur if there were less short-range order. Our predicted ordering is now being tested by x-ray and neutron experiments. This work was done by a student, Li Li, supervised primarily by P. B. Allen.

The second thrust in this period has been on computational prediction of surface structure. Preliminary experiments indicate that a commonly-exposed surface of the GaN/ZnO alloy is the “semipolar” (101bar1) surface. So far we have used GaN as the test case, and have predicted stable surface structures as a function of nitrogen chemical potential. A novel nitrogen-rich structure has been found. This work is in collaboration with Oganov and involves development of a code. The USPEX code for bulk structure prediction is being modified for surface applications. A third area is ab initio molecular dynamics of water interacting with the surface of GaN. These calculations have yielded new insights into the dynamics of water at the interface. In particular, we see thermal equilibrium fluctuations at the surface where an H^+ ion bound to a surface N (there is a complementary OH— ion elsewhere, bound to a surface Ga) migrates sometimes onto an H_2O in the liquid, forming H_3O+, and sometimes onto an OH— , forming a loosely surface-bound H_20. These processes are believed to be significant for the chemistry of solar water splitting. This work was done by Jue Wang, a student, supervised largely by Prof. Fernandez-Serra.

Theoretical Investigations of Nano Bio Structures

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This proposal addresses fundamental issues in nanoscale science and technology, namely the design of nanostructured materials and devices with desired, novel characteristics. The research projects focus on several broad areas: (1) controlled self-assembly of organic clusters on surfaces, (2) investigation of transition-metal/protein interactions, (3) multi-terminal molecular junctions for hybrid devices, and (4) methodology of rare-event simulations. These projects build on the work accomplished during the prior proposal period, which included substantial advances to real-space electronic structure methodology and investigations of (1) I-V characteristics of molecular junctions, (2) electronic and optical properties of graphene nanoribbons, (3) multistage copper bonding to the prion protein, and (4) aminoacids/Si interfaces. Our newly developed capabilities enable fully quantum-mechanical simulations of solvated systems through a QM/approximate-QM methodology at much reduced cost, and efficient treatment of first-row and transition metals through ultrasoft pseudopotentials implemented in real space. Our improved real-space multigrid method is capable of simulating the dynamics of systems containing thousands of atoms on DOE's leadership-class massively parallel supercomputers.

Effective Medium Theory for Periodic Composites

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This project deals with the effective medium theory for periodic and disordered composites. The effective medium is a homogeneous medium which substitutes the inhomogeneous medium in the long-wavelength limit. The effective medium keeps the main conducting, dielectric or elastic properties of the original medium, but makes the description much simpler. It is widely used in electrodynamics and acoustics for calculation of the properties of a heterogeneous medium, which is a composite of a homogeneous matrix with inclusions of a different material. The inclusions can be either randomly distributed in the matrix, thus forming a disordered system, or can be regularly arranged, making up a periodic structure. In the latter case these structures are called photonic (in the case of dielectric materials) or phononic (in the case of elastic materials) crystals. It turns out that an artificial heterogeneous medium may possess such effective parameters that do not exist for natural materials, and in this case, they are called metamaterials. In the last few years, the metamaterials have been designed and fabricated that possess a negative index of refraction, plasma-like behavior with ultra-low plasma frequency, negative effective mass, high optical and acoustical anisotropy, and selective transparency. Metamaterials are usually structured at the nanometer scale and they help us to overcome the diffraction limit in optics and acoustics, i.e. they let us detect and view objects with dimensions less than the wavelength. On the other hand, metamaterials may hide objects from being detected by radar and/or sonar.

The main outcome result of the effective medium theory are the analytical formulas for the effective parameters, like index of refraction, speed of sound, localization length, etc for a periodic or disordered medium with arbitrary material of the inclusions and the matrix. In the course of this project we will apply our previous analytical results of the effective medium theory to the design of new metamaterials possessing high optical or acoustical anisotropy, low or high absorptivity, and prescribed localization length, etc. In collaboration with the experimental group of Prof. Sánchez-Dehesa from Polytechnic University of Valencia in Spain, we will calculate the effective parameters of the metamaterial and then fabricate them. We will also extend the results of the effective medium theory to dissipative photonic crystals. The goal is to develop recommendations that may increase the efficiency of optoelectronic devices. Low efficiency is related to high Joule losses in the metallic parts of artificial photonic crystals and metal-dielectric plasmonic structures. Regarding the development of the effective medium theory for random systems, we will continue our study of low-dimensional structures with correlated disorder.

In addition, we plan to study electron localization in DNA macromolecules. DNA, being a store of genetic information, is a random two-channel conductor, where electrons are localized due to disordered appearance of the nucleotides – adenine, thymine, guanine, and cytosine. Our goal is to compare the localization length (and thus electrical resistivity) in the coding parts of DNA – exons, with localization in the “junk” parts of DNA – introns. We expect that since these two parts store qualitatively different information, the correlation functions of the DNA texts written in exons and introns are also very different, leading to considerable difference in the correlation lengths. This part of our study may find useful applications in DNA sequencing and detecting mutations using electrical measurements.

CMCSN: Computational Time-Resolved and Resonant X-Ray Scattering of Strongly Correlated Materials

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Basic-Energy Sciences of the Department of Energy (BES/DOE) has made large investments in x-ray sources in the U.S. (NSLS-II, LCLS ALS, APS) as powerful enabling tools for opening up unprecedented new opportunities for exploring properties of matter at various length and time scales. The coming online of the LCLS—a pulsed photon source, literally allows us to see and follow the dynamics of processes in materials at their natural timescales. There is an urgent need therefore to develop theoretical methodologies and computational models for understanding how x-rays interact with matter and the related spectroscopies of materials. The present project is addressing aspects of this Grand Challange x-ray science. In particular, our Collaborative Research Team (CRT) is focusing on developing viable computational schemes for modeling x-ray scattering and photoemission spectra of strongly correlated materials in the time-domain. The vast arsenal of formal/numerical techniques and approaches encompassed by the members of our CRT are being brought to bear through appropriate generalizations and extensions to model the pumped state and the dynamics of this non-equilibrium state, and 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. Alternatively, when the core-valence interactions are strong, one can view K-edge RIXS for example, as the dynamic response of the material to the transient presence of a strong core-hole potential. Unlike an actual pump-probe experiment, here there is no mechanism for adjusting the time-delay between the pump and the probe. However, the core hole predominantly decays via Auger processes, thereby providing an internal time-scale, which limits intermediate-state processes to timescales of a few femtoseconds. In this way, RIXS and the relaxation dynamics it harbors through the coupling of the core-hole to valence excitations, make RIXS of direct relevance to the time-domain interests of this proposal. Accordingly, a number of activities directed at modeling K-, L- and M-edge RIXS in correlated materials are being pursued by our CRT.

Our research effort 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 photoinduced effects such as energy conversion in photosynthesis and solar cell applications, and thus impacts the basic science for energy needs.

Electronic Structure, Spectroscopy, and Correlation Effects in Novel Materials

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This project is targeted on modeling and understanding electronic structure, spectroscopies, and correlation effects in a variety of novel materials of great current interest. Spectroscopies resolved highly in momentum, energy or spatial dimensions are playing a key role in unraveling the nature of the ground state and excitation properties in wide classes of novel materials. The seminal insights thus obtained are of critical importance not only for answering some of the great fundamental questions facing condensed matter physics and materials science today, but also for understanding and thus helping to design and develop new materials with desirable properties (e.g., topological insulators and other exotic forms of quantum matter), which will continue to be the key to the survival of mankind and its energy needs as a technological society long into the future.

However, spectroscopies do not provide a direct map of electronic states, but act as a very complex 'filter' or 'mapping' of the underlying spectrum. This connection between electronic states and measured spectra—called the 'matrix element effect'—is in general an extremely complex function of the phase space of the experiment (e.g., energy/polarization of photons and the momentum/spin of the electron in photoemission), presenting both a challenge and an opportunity. A good understanding of the matrix element effect is crucially important not only for fully exploiting various spectroscopies, but also to ascertain optimal regions of the experimental phase space to zoom in on states of the greatest interest.

So motivated, the PI is pursuing techniques for realistic treatment of electronic spectra of a wide variety of materials, which serve as a prelude to formulating and implementing methodologies for making direct connection with various spectroscopies. This project is concerned specifically with, angle resolved photoemission (ARPES), resonant inelastic x-ray scattering (RIXS), scanning tunneling microscopy/spectroscopy (STM/STS), magnetic and non-magnetic Compton scattering, and positron annihilation spectroscopy related issues, including some work on neutron scattering and optical spectra. Specific systems involved are cuprates, pnictides, topological insulators, manganites, magnetite, and nano-particles. Our goal is to exploit the strengths of various spectroscopies to piece together the most complete picture of electronic states in systems of great current interest, enabling direct and sharpened confrontations with theoretical models, and also to help advance the reach of various spectroscopies.

Within the framework of the preceding overarching unifying goal, the ongoing/proposed research contains many new directions involving development/implementation of new methodologies, enabling the PI to attack new classes of problems, as well as work on new materials. In particular, we have moved from LDA to 'beyond LDA' schemes and to a new far more comprehensive level of modeling the underlying electronic spectrum, and to developing/implementing methodologies needed for unfolding associated matrix element effects in ARPES, STM/STS, RIXS, magnetic Compton, positron-annihilation and other spectroscopies. In this way, it has become possible for us to address for the first time issues related to the physics of self-energy corrections, superconducting orders, pseudogaps, impurities and nanoscale heterogeneities, and how matrix element effects can enhance/suppress related signatures in various spectroscopies. New materials classes include recently discovered pnictides and topological insulators, requiring increased focus on the treatment of alloying and relativistic effects. New spectroscopic techniques in ongoing/proposed research include addressing magnetic excitations through neutron scattering, doping evolution of spectral weights through optical spectra, and extensions/generalizations in ongoing work on other spectroscopies of interest to this proposal.

Notably, with the current and planned high-resolution beamlines at various DOE supported facilities, tremendous amounts of data are becoming available, launching a new era for probing the huge phase space of experiments as a function of temperature, magnetic field, doping level and substitutions on various sites in the normal and the superconducting state. It will be difficult to effectively utilize this powerful instrumentation without parallel theoretical efforts of the sort being pursued here to develop sophisticated modeling methodologies, including key effects of strong correlations, electron-phonon coupling, and various nano-scale heterogeneities. The proposed program will help fill this critical gap by continued development of increasingly sophisticated theoretical tools for analyzing and interpreting the most important highly resolved spectroscopies in wide current use today.

Dynamical and Non-Equilibrium Effects in Higher-Order and Pump and Probe X-Ray Scattering

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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. This is generally followed by a cascade of intersystem crossings. Examples are spin crossover phenomena in divalent iron and ruthenium complexes. In the ground state, divalent Fe is in a low-spin state. Illumination by light causes a charge transfer to the ligands, followed by a cascade of intersystem crossings, turning the singlet configuration into a high-spin state. The high-spin state has a temperature-dependent decay time back into the low-spin state that can vary from nanoseconds up to days. Recently, we have developed mechanisms for ultrafast intersystem crossings in these systems (*Physical Review Letters* 104, 067401 (2010), Phys. Rev B. 82, 075124 (2010)). We have extended these to describe pump-probe spectroscopy in Ir(bpy)3. 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 non-equilibrium dynamics. This work has been submitted.

In the past decade, Resonant Inelastic X-ray Scattering (RIXS) has made remarkable progress as a spectroscopic technique. This is a direct result of the availability of high-brilliance synchrotron X-ray radiation sources and of advanced photon detection instrumentation. The technique's unique capability to probe elementary excitations in complex materials by measuring their energy-, momentum-, and polarization-dependence has brought RIXS to the forefront of experimental photon science. In collaboration with four others, a review was written on both the experimental and theoretical RIXS investigations of the past decade, focusing on those determining the low-energy charge, spin, orbital and lattice excitations of solids (*Review Of Modern Physics 83, 705* (2011)). The presence of dd excitations in K-edge resonant inelastic x-ray scattering in the 1s to 4p region of transition-metal compounds and their excitation mechanism was established through measurements of NiO and $NiCl_2$. It is demonstrated that the valence excitations are due to the interaction between the excited 4p electron and the 3d valence electrons. This work was done in collaboration with Steve Cramer's group (LBNL, UC Davis) and promises interesting applications in the study of enzymes (*Physical Review B. 83*, 045101 (2011).).

In a collaboration with Jeroen van den Brink (IFW Dresden) and Luuk Ament (University of Leiden), it was shown that RIXS is can also excite phonons. RIXS can provide direct, element-specific and momentum-resolved information on the electron-phonon (e-p) coupling strength. Our theoretical analysis indicated how the e-p coupling can be extracted from RIXS spectra by determining the differential phonon scattering cross section (Europhys Lett. 95, 27008 (2011)).

Research related to X-ray spectroscopy on transition-metal oxides, in particular looking at the effects of confinement and extreme conditions (such as pressure) have been performed. In particular, we have studied the effects of quantum confinement in thin layers and heterostructured nickelates (Phys. Rev. B 84, 125137 (2011)). Closely related to that is the interpretation of X-ray linear dichroism on thin layer of nickelates measures by Chakhalian, Freeland and co-workers (Phys. Rev. R83, 161102 (2011). We have also worked on the change in exchange interactions under pressure with Daniel Haskel (Phys. Rev. B R84, 100403 (2011)).

Electronic Structure and Novel Properties in Complex Oxides and Hetero-Interfaces

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This project is focused on the elucidation of several of the striking, diverse and challenging phenomena observed in perovskite hetero-interfaces, semiconductor hetero-bonded interfaces, as well as in the manganites. More specifically, we will focus on (1) interface electronic structure and possible high TC superconductivity in heterobonded metal-semiconductor superlattices, including superconductivity; (2) $LaAlO_3/SrTiO_3$ hetero-interfaces, including polarity and defect effects (role of oxygen vacancies), and possible superconductivity; (3) structure and magnetic order in bilayer manganites well known for their colossal magnetoresistance effects, including orbital mixing, charge ordering, and nesting in bulk, the energetics of microstructure, effect of pressure, optical properties, and the structural stabilization of their magnetic surfaces. (Several experimental groups, with which we are in close collaborative contact notably at Argonne National Laboratory and Oak Ridge National Laboratory, are actively investigating these systems and we expect our joint efforts to lead to important breakthroughs.); (4) epitaxial structure of Mn perovskites with $La_{1-x}Sr_xMnO_3$ compositions; (5) electric field-induced magnetism phenomena at surfaces and interfaces; and (6) magneto-electric effects in 5d iridates and topological insulators.

We employ our state-of-the-art, first-principles, all-electron full-potential linearized augmented plane-wave (FLAPW) method. New methodologies/functionalities incorporated into our FLAPW method/code - now fully and efficiently parallelized with good scalability (runs up to 1280 processors, so far) include (1) our unique self-consistent screened exchange-LDA approach for accurately determining excited states and optical properties without artificial parameters; (2) intra-atomic noncollinear magnetism with no shape approximation for the magnetization density (here, density functional theory is treated with a density matrix with 2x2 components of the charge and magnetization densities, which allows the magnetic moment direction as well as the magnitude to vary continuously all over space); (3) the self-consistent linear response determination of lattice dynamics/phonons purely from first-principles; and (4) inclusion of electric field effects into the FLAPW formalism.

Theory of Hydrogen Storage in Complex Hydrides

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General adoption of hydrogen as a vehicular fuel depends critically on the ability to extract hydrogen at sufficiently rapid rates. The DOE targets for hydrogen storage systems are very challenging and cannot be met with existing materials. Recent experimental and theoretical studies have identified several new complex hydrides with thermodynamic properties and material storage capacities approaching and, in some cases, surpassing the DOE system targets. However, all these materials suffer from poor kinetics and revolutionary new advances are needed to realize their promise as on-board H_2 storage materials. This can only be achieved through an improved understanding of the microscopic driving forces and kinetic factors controlling the rate of phase transformations involved in hydrogen release.

In this project, 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 effect of defects and nanoscale catalysts in achieving fast kinetics and reversibility will be elucidated at the atomic level, and various strategies for enhancing the kinetics will be pursued, such as searching for low-melting-temperature eutectic liquids and design of heterogeneous nucleation centers.

The proposed work is expected to meet the broader impact goals for DOE-BES, leading to (1) improved fundamental understanding of the factors that control the (de)hydrogenation kinetics and thermodynamics of a large variety of materials, (2) a significant advance in the rational design of hydrogen storage materials with superior kinetics, and (3) ultimately, the accelerated development of improved hydrogen storage systems.

Large Scale Quantum Simulations of Disordered Transition Metal Oxides: Self-Organized Inhomogeneous Nanoscale Structures

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(I) EMERGENT GRANULARITY ON THE MESO-SCALE AND THE SUPERCONDUCTOR-INSULATOR TRANSITION

We have obtained the phase diagram of the disorder-driven superconductor–insulator quantum phase transition using quantum Monte Carlo simulations that treat, on an equal footing, inhomogeneous amplitude variations and phase fluctuations, a major advance over previous theories. Our simulations and in-depth analysis have given new microscopic insights into the nature of the superconducting and insulating phases and the mechanism driving the transition and allowed us to make testable predictions for local spectroscopic probes. Among our significant results are (1) the energy gap in the density of states survives across the transition, (2)coherence peaks exist only in the superconductor, (3) a characteristic pseudogap persists above the critical disorder and critical temperature, in contrast to conventional theories, and (4) vey surprisingly, the insulator has a two-particle gap scale that vanishes at the transition despite a robust single-particle gap.

(II) NOVEL MODULATED SUPERCONDUCTING PHASES IN THE PRESENCE OF DISORDER AND MAGNETIC FIELDS IN TRANSITION METAL OXIDES

In a collaboration between the experimental group of Phil Adams (LSU) and my theoretical group, we have resolved the long standing mystery of excess sub-gap states measured in tunneling in disordered superconducting films in a Zeeman field, previously unexplained by standard BCS theory. We provide a natural explanation of these excess states in terms of a novel disordered Larkin-Ovchinnikov phase that occurs near the spin-paramagnetic transition at the Chandrasekhar-Clogston critical field. The disordered Larkin-Ovchinnikov superconductor is characterized by a pairing amplitude that changes sign at domain walls. These domain walls carry magnetization and support Andreev bound states that lead to distinct spectral signatures at low energy.

In the next phase we are investigating ferromagnetism in multi-orbital systems.

Modeling Dynamically and Spatially Complex Materials

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Structural phase transitions govern the properties of many materials. In titanium, the ductile alpha-phase can transform to a brittle omega-phase -- undesirable for aerospace and medical applications. The transition is both fast -- only small atom motions -- and first-order -- preserving structural integrity. A crucial step in understanding and preventing this transformation is the discovery of its specific atomic pathway.

The course of discovery produced a general procedure for such transitions that occur in many important materials. The effort required not only the development of new potentials (classical and tight-binding) but a range of methods (molecular dynamics and first-principles methods). For titanium, from a thousand possible pathways, a systematic approach, in two steps of increasing complexity, winnowed the list to seven. First-principles calculation showed the energy cost of one pathway was one-quarter that of others. The relative orientation of the alpha and omega phases was consistent with experiments on pressure-driven transitions.

The new pathway allows exploring the effects of alloying elements. First-principles calculations of the relative stability and barrier to the transformation for other alloying elements commonly used in titanium yielded estimates for transformation pressure consistent with experiments.

Preliminary molecular dynamics on large supercells shows the alpha-to-omega transformation occurs at roughly the speed of sound as generally believed. Continuing molecular dynamics studies will confirm the reverse transformation under pressure and a different relative orientation of the two phases in shock wave experiments.

Theoretical Investigations of Single Particle Spectroscopies of Novel Materials

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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.

In recent years, two single-particle spectroscopy experiments – angle-resolved photoemission (ARPES) and scanning tunneling microscopy (STM) – have given invaluable, complementary insights into the properties of these novel materials.

The objectives of this proposal are first, to develop the theoretical framework for analyzing new photoemission experiments—low-energy laser ARPES and two-electron coincidence spectroscopy—on a broad class of materials. Second, we will make quantitative predictions for ARPES and STM experiments on strongly correlated materials using both analytical theory and numerical simulations. Third, we will gain fundamental insights into the novel properties of two classes of materials: the effects of disorder-induced nanoscale inhomogeneity in the high Tc superconducting cuprates, and the metal insulator transition, colossal magnetoresistance and possible electronic inhomogeneity in bilayer manganites.

A significant part of the proposed research is related to experiments being done at several DOE labs. Parts of the work will be done in close interaction with the experimental photoemission group at Argonne. This research is expected to lead to the development of ideas and techniques with broad impacts on the study of complex materials which have the potential of playing a major role in future applications in the areas of energy, in the case of superconductors, and in information technology, in the case of novel magnetic materials.

Change, Spin and Heat Transport in Low-Dimensional Systems

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The main theme of the proposal is to study spin, charge and heat transport in low dimensional nanostructures. We have been very active in research in 2011 with 9 publications supported by DOE. The following summarizes two representative works.

(1) SPIN SUPERCONDUCTOR IN FERROMAGNETIC GRAPHENE

We show a spin superconductor (SSC) in ferromagnetic graphene as the counterpart to the charge superconductor, in which a spin-polarized electron-hole pair plays the role of the spin `Cooper pair' with a neutral charge. We present a BCS-type theory for the SSC. With the `London-type equations' of the super-spin-current density, we show the existence of an electric `Meissner effect' against a spatial varying electric field. We further study a SSC/normal conductor/SSC junction and predict a spin-current Josephson effect.

(2) ENHANCEMENT OF THE THERMOELECTRIC FIGURE OF MERIT IN A QUANTUM DOT DUE TO THE COULOMB BLOCKADE EFFECT

We study the effect of interactions on the time reversal invariant topological insulators in four and three spatial dimensions. Their topological indices are expressed by the interacting Green's functions. Under the local self-energy approximation, we find that interaction could induce nontrivial frequency-domain winding numbers and change the topological classes of the system. Our results suggest that the topological phases could be destroyed without developing long range orders.

Theory of Topological Quantum Numbers in Low Dimensions

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Funding: $125,000

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 determining the range of applicability and the robustness of the topological behavior. The best known such phase of matter is the fractional quantum Hall effect (FQHE), 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.

Anharmonic and Thermal Effects Associated with Jammed Solids

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Funding: $120,000

A collection of idealized spheres jam into a disordered solid when compressed at zero temperature. Our work has shown that this jamming transition is singular, in that the number of inter-particle contacts at the transition is exactly the minimum number needed for mechanical stability. In the manner of an ordinary critical point, this singularity controls the harmonic as well as the anharmonic properties of the solid in the vicinity of the transition. Our objective is to address the following questions:

(1) How does the system behave when pushed beyond the harmonic regime so that anharmonic effects become important? Our results have shown that the most anharmonic vibrational normal modes exist 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. What is the nature of the energy-barrier distribution? At the jamming transition, anharmonic effects diverge. How do they evolve as the system is compressed above that transition? How are states that are connected by low energy barriers related to each other?

(2) What is the effect of shear stress on idealized sphere packings? How does one localized rearrangement trigger another to lead to macroscopic failure in the form of a shear band? Can we predict from the harmonic spectrum or the anharmonic response how close a system is to the edge of failure?

(3) What is the effect of temperature? Could the anharmonic quasi-localized modes herald the existence of two-level systems or dynamical heterogeneities? Can the normal modes themselves be enough to produce some of the characteristic properties of low-temperature glasses such as the appearance of phonon echoes? How is the jamming transition related to the glass transition?

(4) 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?

We are performing computer simulations of particles with finite-ranged repulsive interactions at the threshold to jamming. We will also use a variety of other potentials that include long-ranged attractions as well as bond-bending interactions. Equilibrium and nonequilibrium molecular dynamics simulations, Monte Carlo simulations, and numerical minimization techniques will be employed.

We have been able to generalize many of the results for idealized spheres to more realistic systems. Several laboratories, including ones that we collaborate closely with, are providing experimental tests to these ideas. We expect that the studies outlined in this proposal will not only provide theoretical insight to general packing problems, but also reveal the underlying cause of some of the longstanding experimental phenomena found in disordered solids.

Electronic and Piezoelectric Phenomena in Nanostructures

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Funding:	$105,000

This project studies the electronic properties of nanomaterials with a focus on graphene-derived materials, topological insulators and topological semimetals. The work develops and applies new theoretical models to describe the low energy physics relevant to electronic transport and can guide the integration of these systems into electronic, optoelectronic and electromechanical applications.

Presently we are studying the physics of stacked few layer graphenes to understand the effects of rotational disorder in the layer stacking on their electronic properties. The work on topological insulators examines the nonlinear surface screening that results from partial filling of their topologically protected surface states and their small bulk bandgaps. Finally, our work on topological semimetals explores physical realizations of a fully three dimensional Dirac semimetal, i.e., systems which are described by a three dimensional generalization of the low energy pseudo-relativistic model well studied in single layer graphene. These systems, if identified, will provide the simplest prototypical model of a three dimensional semimetallic material, and potentially provide a platform for interesting many body physics.

First-principles Investigations of the Physics of New Semiconducting Ferroelectrics for Solar Light Absorption and Carrier Separation

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Funding:	$250,000

This research program will use and develop 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 a demonstrated ability to separate carriers. However, nearly all ferroelectric oxides are insulators, making them inefficient for solar photovoltaic applications. The recent upsurge of interest in $BiFeO_3$ (ferroelectric, with band gap of 2.8 eV) as well as materials design of derivatives of $PbTiO_3$ by this PI during the current grant period, have suggested great opportunities for the discovery of new single-phase materials for photovoltaic applications.

CMSN Structure and Dynamics of Water and Aqueous Solution in Materials Science

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Funding:	$215,000

The goal of this computational research team 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 to other U.S. Universities, to National Laboratories and to major international research institutions. This activity initiated with a kickoff workshop held at the Princeton Center for Theoretical Science (PCTS) on Dec 6-8 2010. The second workshop on the series will take place at the Talaris Conference Center in Seattle on February 10-12, 2012. A third workshop will be held at UC Davis in 2013 at the end of the funding period for this grant.

To date the following research highlights can be listed:

(1) The effects of hybrid DFT functionals, of Van der Waals interactions and of quantum nuclei on the structure of liquid water have been investigated. When all these effects are included the pair distribution functions and the structure factors predicted by theory get very close to those extracted from diffraction experiments. Current and future work along these lines should help to better elucidate the implications of these results on major debated issues on the microscopic structure of water.

(2) Hybrid DFT functionals have been found to improve substantially the agreement with experiment of the calculated IR spectra within the harmonic approximation. Future work will help to better understand the role of nuclear quantum corrections on the IR spectra.

(3) The optical and the x-ray absorption spectra of a variety of water systems in condensed phase have been calculated using a COHSEX approach developed at Princeton and a Bethe-Salpeter approach developed at the University of Washington. The systems studied include crystalline ice (with and without proton disorder), liquid water, low-density and high-density amorphous ices. When good structural models (including zero-point motion) and accurate electronic screening models are combined, unprecedented agreement is found between theoretical and experimental spectra. Future work will focus at identifying the microscopic structural information that is behind the observed spectral features.

Density Functional Theory with Dissipation: Transport Through Single Molecules

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Funding:	$105,000

The goal of this project is to provide a framework for realistic calculations of electron transport through molecular wires.

Past work by this investigator, in collaboration with Kieron Burke at the University of California at Irvine, produced a variety of results at the forefront of this field. These results included an entirely new approach to this problem, DFT for open quantum systems, a linear response approach (Kubo formalism) within Time-Dependent DFT, valid in the weak-bias regime, the identification of substantial errors in the current characteristics coming from level misalignment within common DFT approximations, and the use of complex band structure techniques to understand the length dependence of conductances of long organic molecules.

Current work going on at Princeton focuses on the implementation of the GW formalism to molecular conduction. This approach improves substantially the level alignment. Our approach will allow realistic calculations of the transport characteristics of devices consisting of hundreds of atoms in the context of quasi-particle theory. This approach will be used initially in off-resonant calculations within linear response theory and will be subsequently extended to both resonant and off-resonant situations using the master equation approach developed in our group.

Work is also underway to use the master equation approach to investigate dissipative effects in the context of simplified tight-binding models.

TMS: Design Principles for Quantum Hall States

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Funding:	$475,000

This project uses diverse numerical methods combined with new analytic insights to study a variety of systems in the quantum Hall regime, in the hope of uncovering the general principles behind obtaining desired quantum Hall states. Having such principles would be of enormous utility in a program involving topologically based quantum computing which uses non-Abelian quantum Hall states, by providing guidelines for what systems are most likely to provide maximum stability of these states.

Nature has been kind to us in providing a large energy gap that characterizes the fundamental fractional quantum Hall state (1/3). This translates to a short length scale, so that numerical solutions on small system sizes, which can be obtained exactly by numerical techniques, provide good approximations to large sized experimental systems. This is unique among strongly interacting, quantum many-body condensed matter systems. However, the more fragile descendent states, and especially the non-Abelian quantum Hall states have small energy gaps, and thus involve larger length scales; this renders small size calculations to be not accurate enough, and more extensive effort is required for further progress.

Such a project is necessarily ambitious and has become possible because of the enormous strides made both in computational ability in recent years (high memory, fast, multi-core processors) as well as the development of controlled approximation methods, such as Density Matrix Renormalization Group (DMRG). These methods can be used to extend the range of system sizes that can be studied, beyond those that can be tackled using exact diagonalization methods, and thus complement and supplant traditional approaches.

We have used a variety of numerical techniques to address the properties of quantum Hall states in semiconductor heterostructures, and single and multilayer graphene, as well as anisotropic systems. For anisotropic systems, a new theory has been formulated, in which a new transport property called quantum Hall viscosity plays a central role. The theory identifies a unimodular two-dimensional spatial metric that characterizes the local shape of the correlations of the incompressible fluid as the fundamental collective degree of freedom of quantum Hall states, whose quantum fluctuations are controlled by a topologically quantized "guiding-center spin." At a more microscopic level, a family of metric-dependent Laughlin states have been identified, with the original Laughlin wave function (long thought to contain no variational degree of freedom) as a special member of this family. In a parallel effort, we have studied numerically the possibility of realizing universal chiral Luttinger liquid behavior, which has not been seen in semiconductor heterostructures, in graphene-based systems. Future projects are planned to study systems with more complicated electronic structures.

TMS: Defect Modeling Beyond Density Functional Theory

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Funding:	$300,000

Designing new materials with controllable properties is particularly important to the development of low-cost, sustainable, and environmentally friendly energy materials. In the past, first-principles theories have played a key role in this endeavor, and with the rapid increase in scientific computing power such a role only intensifies. However, realizing the vision of true computational materials discovery will require that structural and chemical complexity in real materials must be adequately addressed. Defects play an important role in controlling materials electronic, optical, transport, and interface/surface properties. Therefore, an in-depth understanding of defect properties in solid is critical for rational materials design.

This project aims at developing computational capabilities for accurate predictions of defect properties and their applications to defects in real materials. We target a range of outstanding energy-related defect problems, including impurities and defects in wide-gap materials such as oxides, nitrides and diamond, their fundamental doping limits, interfacial defects between highly dissimilar materials such as inorganic and organic materials, and impurity diffusion. The project addresses these key defect issues by a comprehensive development of more-predictive modeling approach that combines the strengths of hybrid functional, GW quasiparticle, quantum Monte Carlo, and advanced mathematical methods.

Critical Phenomena in Driven Granular Matter: Jamming and Glassy Behavior

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Funding:	$115,000

Large-scale numerical investigations of soft-core interacting particles will be carried out to study the nature of jamming in granular matter and related glassy systems. Physical quantities such as pressure and shear stress will be computed as functions of particle packing fraction, uniform applied shear strain rate, temperature, and system size, for a variety of system dimensions, short-range contact interactions, particle shapes, and substrates. Critical scaling ideas, from the theory of equilibrium phase transitions, will be applied to analyze the resulting data and determine the effect of the jamming transition ("point J") on behavior at finite shear flow and finite temperature. In particular, the relation between point J and glassy relaxation in models of supercooled simple liquids will be studied, with a view towards clarifying the nature of the apparent equilibrium glass transition observed in such systems. Effective temperatures in nonequilibrium driven steady state will be computed, and investigated for universal behavior at the jamming transition. Frictional forces between particles will be added to model more realistic granular materials. These investigations will play an important role in unifying the understanding of behavior in a diverse array of physical systems that undergo transitions from flowing liquid-like states to rigid but structurally disordered states, including granular materials, "soft matter" systems such as colloids and foams, and glass forming liquids. These investigations will also help in understanding the applicability of concepts and methods from equilibrium statistical mechanics to the realm of nonequilibrium systems and driven steady states.

CMSN: Computational Design of Fe-based Superconductors

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Funding:	$245,000

Our research seeks a fundamental understanding of the solid state phases elements of the actinide series, as well as compounds and alloys containing them, using computational electronic structure tools based on extensions of the Dynamical Mean Field Theory (DMFT). Simplified physical pictures and phenomenological models of the various phases of these elements and their electronic structure - which in turn can be predict new experiments - are constructed utilizing parameters which can be related to the results of first principles DMFT calculations.

Spin Driven Phenomena in Strongly Correlated Materials

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Funding:	$125,000

Our understanding of the role of magnetic moments as the driver for new kinds of correlated electron behavior is in a state of rapid transformation. Recent experiments highlight new kinds of superconductors, metals and insulators, in which magnetic moments provide the fabric for novel electronic behavior. The science behind these phenomena has an important role to play in the materials and devices of the future. The three research topics in this proposal involve a study of how spins transform electronic behavior in d-electron and f-electron materials. To this research, we bring a range of new insights and techniques acquired during the past funding cycle through the study of the simplest electronic spin systems - quantum dots.

Actinide-based superconductors with elevated transition temperatures. The discovery of two new heavy electron superconductors, in which singlet superconductivity condenses out of a Curie paramagnet of dense, yet unquenched magnetic moments, provides us with remarkable evidence for a new class of superconductor in which localized moments play a direct role in the superconducting condensation process. We seek to develop a detailed theory of these new materials, using the concept of composite pairs to explain why they give rise to heavy electron superconductivity at elevated transition temperatures.

High spin dopants in iron-based semiconductors FeSi and FeGe. New kinds of spin physics are also evident in highly correlated insulators. The narrow gap insulators FeSi and FeGe, long thought of as a kind of highly renormalized “silicon.” have been found to exhibit a new kind of doping behavior in which Mn or Co dopants form high spin-1 or spin-3/2 moments that transform the nature of the metal insulator transition. This new physics, driven by the effects of strong Hund’s interactions, is of great interest in the context of magnetic semiconductors and the newly discovered iron-based pnictide superconductors. We will develop a theory for this new doping mechanism, based on the idea that Hund’s coupling drives a transition to high-spin dopants which incompletely screen in the metallic state, transforming the nature of the doped metallic state.

Atomistic Study of Ultrafast Dynamics in Multifunctional Materials in Bulk and Nanoforms

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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 which include imaging and characterization, detection of hazardous substances, environmental monitoring, radio astronomy, covert inter-satellite communications, as well as biological and medical applications. However, despite the many advantages that it offers, the THz region is still poorly understood and underutilized nowadays. As a result it is often called “THz gap.” 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:

Objective (1) – Develop a set of computational tools that allows accurate modeling of THz properties of ferroelectrics and magnetoelectrics at an atomistic level. Such a unique simulator will have capabilities that are unmatched by any currently available approach and will include the capability to simulate (a) bulk and nanoscale ferroelectrics and magnetoelectrics; (b) static and dynamical properties, including ultrafast dynamics; (c) 0 Kelvin and finite temperature; and (d) large systems (~ 10^6 of particles).

Objective (2) – Explore, predict, and understand at an atomistic level the fundamental dynamical properties of ferroelectrics and magnetoelectrics at THz using our new simulator.

Objective (3) – Explore, predict, and understand at an atomistic level the physical response of multifunctional nanoscale materials to ultrafast external excitations such as temperature fluctuations, electric and magnetic fields, pressure, and heat/energy pulses.

The potential outcomes of this research include (1) state-of-the-art computational tool for modeling of THz properties of nanoscale multifunctional materials; (2) deep atomistic understanding of ultrafast dynamics in such materials; (3) fundamental understanding of mechanisms that drive the response of polarization, magnetization to the ultrafast electric, magnetic fields, temperature, pressure, stress, and strain fluctuations which will reveal their potential for ultrafast energy conversion. Ultimately, this project may lead to the discovery of materials for THz nanogenerators, THz nanodetectors, pressure, temperature electric and/or magnetic field nanosensors, ultrafast and ultra dense non-volatile memory that allows ultrafast picosecond non-destructive read-out.

Theoretical Studies of Graphitic Nanostructured Materials Interactions

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Long ranged interactions, such as van der Waals and Casimir forces, are of fundamental importance for understanding the basic science of nanostructured graphitic materials. Such interactions are responsible for how graphitic systems interact between each other and with other materials. The focus of this project is carbon nanotubes, graphene, and graphene nanoribbons interactions. The objectives are to investigate how unique properties stemming from the dimensionality, curvature, and honeycomb carbon atom arrangement influence the van der Waals/Casimir forces. Our investigations so far show that van der Waals/Casimir force description based on a two-body Lennard-Jones potential maybe a simple way to describe experimental results involving separation and relative motion of graphitic nanostructures; however, this interaction is much more complex since it is directly influenced by the dielectric and magnetic response of the involved objects.

An important result from this work shows that carbon nanotube chirality signatures, such as strength and frequency locations of optical excitation peaks, can change the strength of the force significantly even though the actual radial size is similar. Interestingly, graphene long ranged interaction at the quantum limit with other graphenes or other materials is extremely weak; it is almost two orders of magnitude weaker than the correspondent force between two metals, but it has the same distance dependence. Furthermore, the presence of edges and their relative orientation turn out to be of crucial importance in interacting graphene nanoribbon. This project also facilitates theoretical investigations related to uncovering how materials with unusual dielectric and magnetic response properties interact with graphitic structures. Such studies allow us to uncover unusual dependences as well as finding ways to manipulate the magnitude and sign of the Casimir force.

Quantum to Classical Crossover of Collective Modes in Correlated Matter

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As human manipulation of matter reaches the nanoscale, new challenges emerge in the understanding of complex systems. The behavior of correlated materials at the classical-to-quantum interface is one such challenge. As the relevant length and energy scales of structures enter the domain where quantum fluctuations become manifest, the crossover is far from smooth, which is evidenced by peculiar collective resonances. In this project, we explored the quantum-to-classical interface in atomic and molecular clusters of strongly interacting electronic systems. Our aim was to understand, and hence to control, their physical response, based on fully quantum-mechanical models which capture accurately the essential physics of the crossover regime, and particularly of the relevant collective modes. The evolution of these modes as a function of the system shape, of applied external fields, and of non-equilibrium driving, is the key to the properties of nanoscale devices.

We focused specifically on two representative examples of the classical-to-quantum crossover: for a system with only spin degrees of freedom, the transition of magnon excitations in antiferromagnetic clusters; and for a system with charge degrees of freedom, the evolution of plasmon modes in metallic clusters. Here it is essential to consider in addition the possibility of a coexistence of typical classical and quantum response functions in structures of arbitrary geometry, and the identification of those signatures of quantum-mechanical response which are precursors of classical behavior. This information leads to an understanding of how collective effects can be controlled, protected and enhanced in such systems.

To address these questions, we developed and applied techniques suitable for the analysis of correlated clusters in real space, including for magnetic systems the stochastic series expansion Quantum Monte carlo method, exact numerical diagonalization, real-space spine wave theory, and an Ising mean-field theory. For metallic clusters with Coulomb interactions, we developed a non-local response theory, in which non-locality is the critical ingredient required for an adequate description of nonlinear dielectric properties in systems with variable size and shape in the presence of an oscillating applied electromagnetic field. The computational hardware for the execution of this project was provided in large part by the high-performance supercomputer cluster at the University of Southern California. Moreover, we used the DOE supercomputer facilities at NERSC and at ORNL.

Thermomechanical Properties of Thin Films and Membranes of Functionalized Nanocrystals and Nanowire Arrays: Multimillion-to-Billion Atom Simulations

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Funding:	$180,000

This project focuses on modeling and simulation of thermomechanical properties of a new class of thin films and membranes consisting of inorganic cores of nanocrystals or arrays of nanowires capped by organic molecules. Recent experiments have shown that the flexibility with which organic spacers endow inorganic nanoparticles with new functionalities allows easy tailoring of electrical, optical, and thermomechanical properties of these hybrid nanostructured materials. This is rapidly expanding the technological uses of inorganic nanocrystals and nanowires from white light sources, ultrathin solar cells, and photodetectors to high-resolution pressure sensors and separation membranes.

We will perform multimillion-to-billion atom molecular dynamics (MD) simulations based on quantum mechanically informed forces to investigate interfacial structure and thermomechanical properties including adhesion and delamination, viscoelastic/viscoplastic behavior, and fracture in the following hybrid systems: (1) thin films of cadmium selenide nanocrystals capped by trioctylphosphine oxide (TOPO)/trioctylphosphine selenide (TOPSe), (2) monolayer membranes of close-packed dodecanethiol-ligated gold nanocrystals, and (3) functionalized ZnO/CdSe and ZnO/Au core/shell nanowire arrays in organic matrices. We will study the nature and strength of bonding between the cores and ligands and interactions between ligands on neighboring cores as a function of the size of nanocrystals and the aspect ratio of nanowires. We will compute stresses and strains at core/ligand interfaces and determine why residual stresses cause delamination and cracking above a certain film thickness. We will investigate elastic and plastic responses of these systems with nanoindentation simulations.

The proposed research will be carried out with a scalable parallel and distributed computational framework for: (1) multi petascale simulations with quantum-level accuracy, (2) multimillion-to-multibillion atom MD simulations based on quantum mechanically informed reactive force fields to reach micrometer length scales, and (3) accelerated molecular dynamics to reach microsecond time scales. Automated model transitioning will be employed to embed higher fidelity simulations concurrently inside coarser simulations only when and where they are required.

Innovative educational and training activities have been established to enrich our research program. These include a dual-degree program offering students the opportunity to obtain a Ph.D. in the physical sciences or engineering and an M.S. in computer science. Dual-degree students are also offered research-training opportunities through collaborations with experimentalists at the Spallation Neutron Source at Oak Ridge and the Advanced Photon Source at Argonne, and with computational scientists at petascale computing facilities at Argonne, Lawrence Livermore, and Los Alamos Nat'l Labs.

We will test the metascalable computational framework on our computing infrastructure, which includes a 2,048-processor Linux cluster in our Collaboratory for Advanced Computing and Simulations and an 8,000-processor Linux cluster at USC. For visualization, we have a 14'x8' high-resolution tiled display and an immersive and interactive virtual environment, ImmersaDesk. Production runs will be made on the IBM BlueGene/P computer at Argonne and the Jaguar at Oak Ridge through DOE's INCITE program.

We will collaborate with scientists at DOE laboratories--Dr. Roger Dejus and Dr. Paul Messina at Argonne and Dr. Alexander Kolesnikov at Oak Ridge.

First Principles Based Simulation of Hydrogen Interactions in Complex Hydrides and Other Hydrogen Storage Materials

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Students:	2 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding:	$164,000

Light-metal complex hydrides have attracted great attention as potential hydrogen-storage materials. Over the past decade, tremendous efforts have been put into improving their storage capacity and adsorption/desorption kinetics. While significant progress has been made in engineering the catalysts and preparing the advanced storage materials over the past few years, hydrogen storage remains a major obstacle in transition to a hydrogen economy. Developing a practical hydrogen storage material requires a detailed understanding of the intrinsic hydrogen-metal bond strength and the effect of local reaction environment. Computational chemistry and molecular simulation offer excellent complements to experimental studies. We are developing a multiscale approach to model desorption and adsorption of hydrogen in complex hydrides and other hydrogen storage materials. We have used density-functional-theory quantum chemical calculations to study the structure and the interactions of hydrogen in these materials. Structures as well as reaction energetics were investigated for bulk materials and finite-sized particles. We analyzed the crystal structures of LiAlH4, NaAlH4, KAlH4 as well as LiBH4 and determined the stability of different crystal surfaces of these hydrides. We also studied the energetics of hydrogen desorption from the surfaces by creating hydrogen vacancies on the surfaces. In Ti-doped NaAlH4, we identified a complex TiAl3Hx as a precursor state for forming TiAl3 that was observed experimentally. The existence of TiAl3Hx complex structures has been confirmed by an independent experimental study. We proposed the role of the complex structure in reversible hydrogen desorption/adsorption in Ti-doped NaAlH4. We further explored the structures of doping other 3d transition metals in NaAlH4 as well as the interaction of doped transition metal with the Al-H bonds in NaAlH4. The roles of the complex structure formed with the doped transition metal in reversible hydrogen release/uptake have been proposed. We started to build a database for the next step – kinetic Monte Carlo simulation – by determining a number of key reaction barriers for hydrogen transportation in the hydride and for desorption/adsorption.

Strongly Correlated Electron Systems

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$75,000

In collaboration with Thomas Durakiewicz and John Joyce at Los Alamos National Laboratories, the PI will investigate the origin of kinks recently found in angle resolved photoemission experiments on the antiferromagnetically ordered compound USb_2 and UPd_2Al_3. Kinks in the dispersion relation are usually found when bands cross the Fermi energy and are attributed to the effects of collective excitations. For USb_2, kinks are found in bands which do not cross the Fermi surface. The origins of these kinks are to be examined. The effects of both electron-phonon coupling and coupling to antiferromagnetic spin fluctuations are to be considered. The asymmetry, line width, and the temperature dependence of the spectra will be investigated. In UPd_2Al_3, which is a heavy fermion metal, a temperature-dependent hybridization gap has been observed in the density of states slightly offset from the Fermi-surface. The origin of the temperature-dependence will be investigated. The occurrence of quasiparticle peaks and pseudo and hybridization gaps in the hidden order compound URu_2Si_2 are also to be studied.

Recently, Jason Lashley and co-workers at Los Alamos National Laboratories and the PI, have investigated a number of materials which exhibit martensitic transitions. It is to be investigated whether the magneto-acoustic oscillations observed in AuZn are due to the effect of Landau quantization on the dielectric constant through the pair-potential or whether these oscillations are attributable to the effects of three or higher body interactions. The weak first order or second-order nature of the transitions in AuZn, V_3SI and SnTe and is not understood. The effect of applied magnetic fields on the transition temperature The recently discovered change in order of the martensitic transition in AuZn alloys and V_3SI will be studied in the context of ferroelastic or screened ferroelastic materials. The collective modes of incommensurate transitions in three-dimensional materials such as Ni_2MnGa or alpha-uranium are also to be investigated using diagrammatic many-body techniques. Experimental manifestations of these modes, other than sliding charge density waves, are to be examined. The effects of long-ranged Coulomb interactions are to be considered.

The anomalous phonon spectra observed in alpha-uranium, found by Mike Manley of Lawrence Livermore Laboratories, is to be investigated theoretically. The above mentioned group found a new mode above 45 K. It has been proposed that this new mode could be due to either soliton-like localized modes, or due to breather excitations in which the phonons couple resonantly to valence fluctuations. These theoretical models and their experimental manifestations are to be investigated theoretically. These studies will be extended to plutonium, and many-body effects will be taken into account. In addition, we shall theoretically investigate the Intrinsically Localized Modes found in NaI by Manley et al. through inelastic neutrons scattering experiments.

Theory of Magnetic Heterostructures on the Nanometer Scale

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Funding:	$148,000

In the renewal of our project we plan to expand into new directions, especially in the physics of helical magnets. They have attracted a great deal of attention in recent years because of the strong interaction between the magnetic and electric subsystems. Our interests are focused on topological aspects of these systems: new topological defects like vortex domain walls, ½-vortices etc. that can interact to electrons through the Berry field and change their transport and magnetic properties. In the multiferroics these defects carry electric charge and can be manipulated by an external electric field. Near the phase transition to the paramagnetic phase the gauge field of the fluctuating order parameter may completely suppress the Fermi excitations causing the metal to enter a non-Fermi-liquid phase.

We plan to study hydrodynamic effects in spin-wave condensates, especially in those obtained by pumping on ferromagnetic systems (Yttrium-Iron garnet). We expect that the “superfluid’ spin current can be excited by the gradient of magnetic field and that heat can propagate as a wave in such systems. Super-thermal conductivity can be expected as well.

A very active field in modern magnetism is the study of the spin torque generated by an electric current. We will study microscopic mechanisms for the spin torque acting on the helical structures and their topological defects. In parallel we will develop a general phenomenological approach based on irreversible thermodynamics trying to take in account the interaction of the magnetic system not only with the electron liquid, but also with phonons and with the inhomogeneous fields that are important in thin magnetic films.

We will continue the study of electronic spin resonance in semiconducting quantum wires started in previous project. Our purpose is to develop the theory of such resonance in the interacting electron (Luttinger) liquid. We also plan to take in account more realistic models of contacts between quantum wire and leads, and study energy and entropy balance in the electric circuit. Together with the search for the most appropriate materials, these studies will help in finding optimal regimes for the resonance.

As an outreach activity we plan to prepare for publication some lecture notes on semiclassical and adiabatic approximation in Quantum Mechanics, to place materials of the course “Symmetry, Order and Disorder” on the official website, to popularize the modern Condensed Matter Physics among High School students, and to develop educational materials on modern and classical physics, for publication and to be placed on a public website.

TMS: Theory and Simulation of Defects in Oxide Materials

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Funding:	$135,000

Oxide materials serve a crucial role in modern electronics, information technology and energy applications. For example, the development of better high-k and low-k dielectric materials are important to allow a continued scaling of electronic devices. However, improving the development devices will require a better understanding of the role of defects as they often play a deleterious role in the performance of current dielectric materials, especially at small or confined dimensions. Understanding the mechanisms of diffusion, optical properties and doping of electronic materials across all length scales is a decidedly open area of research.

To address these areas of research, we draw on expertise in areas such as the materials physics of devices, chemical engineering, materials science, computational physics, numerical analysis and computer science. Our team develops and implements numerical methods specially crafted for examining defects in oxides. Understanding the physical nature of these defects will require us to consider disparate length scales and new theories to address systems that may be highly correlated. We will also need to address both applied and fundamental issues intimately related to both ground state and excited state properties.

Specifically, we use methods based on pseudopotentials and density functional theory, including LDA+U for correlated systems, to examine ground state properties. We consider time dependent density functional theory and GW/Bethe-Salpeter methods to examine excited state properties.

Transport and Collective Properties of Semiconductors and Graphen Overlayers

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Sr. Investigator(s):	Niu, Qian, TEXAS, UNIVERSITY OF Zhang, Zhenyu, TENNESSEE, UNIVERSITY OF
Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$205,000

We have continued our research on the electronic and transport properties of graphene systems, topological insulators (TI), and magnetic nanostructures in year 2011with the financial support of DOE grant DE-FG03-02ER45958 from the Division of Materials Science and Engineering. Eighteen papers have been published in referenced journals (including four in *Phys. Rev. Lett*. and two in *Nano Lett*.), four papers are in press (to appear in *Phys. Rev. Lett*. and *Phys. Rev. B*), and nine papers are under review. Specific areas of study are listed below.

Graphene systems:

- Engineering Rashba and exchange fields in monolayer graphene
- Rashba-induced topological states in gated Bilayer graphene
- Zero-bending resistance of topological confinement states in crystallized bilayer graphene
- Broken symmetry states in bilayer graphene
- Graphene growth and functionality

Topological insulators:

- Realizing tunable Chern number quantum anomalous Hall effect in topological insulators
- Spin-dependent Disorder Scattering in Anomalous Hall Effect
- Magneto-Optical Faraday and Kerr Effects in Topological Insulator Films and in Other Layered Quantized Hall Systems
- Quantum Hall Superfluid in Topological Insulator Thin Films

Growth characteristics of nanostructures:

- Quantum tunability of plasmon in nanoscale
- Electronic growth and novel quantum states in reduced dimension
- Functionality optimization based on atomistic growth energetics and kinetics

Transport and Interactions in Chiral Electron Systems

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Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$110,000

Physics of chiral electron states (i.e., the states whose properties depend on the direction of electron propagation) currently represents the forefront of condensed matter physics. Such states exist in a variety of practical realizations: two-dimensional electron gas in carbon nanotubes, semiconductor quantum wells with spin-orbit interaction, Dirac fermions in graphene, topological surface states in e.g., BiSb compounds, interface superconductivity in LaAlO structures, etc. While the first three systems have been attracting worldwide interest of both theorists and experimentalists in recent years, the other two systems are newly discovered and possess many new exciting properties that are yet to be addressed. We investigate the physics of such novel chiral electron systems. As far as the fundamental physics is concerned, our main objective is to study transport phenomena and the effects of electron-electron interactions from a general perspective of elucidating features common to various chiral systems. Specific physical phenomena addressed include spin behavior near boundaries of 2D electron gas and topological insulators, the effects of interactions and strong electric field on conductivity of graphene, plasmon properties of graphene p-n junctions, and intersubband absorption in metallic nanotubes.

Driven Magnetic Flux Lines in Disordered Superconductors: Relaxation Towards Equillibrium and Nonequillibrium Stationary States

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Students: 0 Postdoctoral Fellow(s), 4 Graduate(s), 1 Undergraduate(s)
Funding: $150,000

The physics of interacting vortex lines subject to strong thermal fluctuations and point-like or extended disorder is amazingly complex and has been a major research focus in condensed matter physics. A thorough understanding of the equilibrium and transport properties is required to render these materials amenable to optimization with respect to dissipative losses, especially in high magnetic field applications. Investigations of vortex phases and dynamics have in turn enriched condensed matter theory. Specifically, vortex matter driven by an external current through a background of pinning centers represents a prominent model system for studying intriguing novel emergent phenomena that arise away from thermal equilibrium. An appealing feature of disordered magnetic flux line systems is their straightforward experimental realization which allows direct comparison of theoretical predictions with actual measurements. Yet neither the relaxation mechanism towards nor fluctuations in the resulting equilibrium and nonequilibrium steady states have been well-characterized theoretically to date.

This research focuses on a thorough numerical investigation of both the driven stationary configurations as well as the hitherto rarely explored out-of-equilibrium relaxation processes, specifically in the `aging' regime. To this end, versatile three-dimensional Monte Carlo and Langevin molecular dynamics simulation codes based on an elastic string representation of the magnetic flux lines are employed, allowing for a large variety of defect configurations. For various pin geometries, steady-state observables as well as two-time relaxation correlation functions are extracted from the simulation data. In addition, nonequilibrium relaxation phenomena are also investigated in benchmark studies of simpler model systems, including driven lattice gases, disordered magnets, and the Coulomb glass. The project has so far involved five graduate students and one undergraduate IAESTE international exchange student. They are familiarized with modern computational methods and sophisticated data analysis, and will acquire advanced mathematical tools developed in nonequilibrium statistical mechanics.

Quantitative Photon and Electron Spectroscopy Theory

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

The primary goal of our DOE Grant is to develop improved theoretical techniques for quantitative calculations of photon and electron spectroscopies over a broad spectrum, spanning the infrared to x-ray energies. Our research plan covers a balance between fundamental theoretical developments and practical implementations. Thus we proposed to develop both advanced computational techniques and codes that can be readily used by others, e.g., through extensions of our well known real space multiple-scattering (RSMS) codes FEFF. Our approach involves two levels of attack: (1) efficient, parameter-free RSMS approaches and (2) first-principles methods based on the Bethe-Salpeter Equation (BSE). Both build on recent developments in the theory of excited states and response functions. In particular achieving our goals requires a quantitative treatment of many body effects that go beyond the independent electron approximation. For method one, we proposed to add new capabilities to the code base in FEFF; for method two, we proposed to develop techniques that build on auxiliary BSE codes from a collaboration with NIST. This collaborative approach is important to facilitate rapid progress, given the limitations in code development that can be accomplished by any small research group. Moreover, linking different codes and making them compatible can be extremely valuable since the combination of methods one and two leads to a hybrid approach that exceeds the capabilities of either alone. These goals have largely been met during the course of this grant. A major achievement was an extension of our BSE approach for core-level x-ray spectra [J. Vinson et al., Phys. Rev. B 83, 115106 (2011).] Another is an extension of our RSMS approach for calculations of resonant inelastic x-ray scattering (RIXS) [J. J. Kas et al., Phys. Rev. B 83, 235114 (2011),] which has been selected for the 2011 ESRF Scientific Highlights by the European Synchrotron Radiation Facility. In addition our research accomplishments were recognized by the 2011 Advanced Photon Source Arthur H. Compton Award.

Scientific Editor, Computational Materials Science Network

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$55,000

The Computational Materials Science Network (CMSN) has emerged as an efficient and cost-effective way to facilitate larger scaled computational materials science research. CMSN, currently with six teams assembling diverse sets of researchers (over 145 scientists in all), provides for the collaboration component of the teams thereby enabling interdisciplinary research on broad problems outside the scope of any one individual research group. CMSN would be seriously hindered without an administrator helping to coordinate its activities. The CMSN administrator organizes meetings, publishes and maintains the CMSN website, publishes a periodic newsletter, facilitates information exchange across the network, serves as a DOE liaison, and communicates CMSN success stories to the larger community. Succinctly, this project deals with the myriad tasks that must be accomplished for CMSN to function.

Electron Coherence and Interactions in Nanostructures

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Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $175,000

Recent rapid progress in nanofabrication and experimental techniques have made it possible to investigate a variety of meso—and nano—scale systems, which were unavailable only a few years ago. Examples include the fabrication of high-quality quantum wires in semiconductor heterostructures, gated nanotube devices, and a number of designs incorporating nanomechanics and electronics. These technological advances have challenged the modern many-body theory to develop new models for their adequate description. The present proposal aims at filling the exposed gaps in knowledge and at facilitating further development of experimental and theoretical physics of nanoscale electronic structures. Specifically, the aims of this project are:

(1) To develop kinetic theory of nonlinear Luttinger liquid within the perturbation theory in the inter-electron interaction.

(2) To explore kinetics of quantum particles in low-energy states at arbitrary interaction strength between the particles confined to one dimension.

(3) To apply the developed theory for understanding the particle-hole asymmetry in the electron kinetics in single-mode quantum wires, fast electron energy relaxation in edge states, and time-resolved measurements of charge propagation in gated carbon nanotubes.

(4) To evaluate the nonlinear dc response to a microwave field of an array of metallic nanorings, as well as a typical single ring; to develop the kinetic theory of electron heating by the microwave field and of the effect of heating on the dc current; and to apply the results to the experiments with nanomechanical cantilevers.

Theory of Nonequilibrium Nanosystems

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Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $92,000

Understanding the dynamics of quantum systems open to an environment represents a formidable challenge for theoretical and experimental physics in the XXI century. Even in cases where the system has trivial dynamics (such as a two-level system), coupling the system to an environment immediately results in a more refined and stimulating model. While much is understood about systems at or near equilibrium, scientists are just beginning to uncover the basic principles governing systems far from equilibrium. As a matter of fact, when energy is continually supplied to systems with many interacting constituents, the outcome generally differs strikingly from the unchanging state that characterizes equilibrium. Breakthroughs in this area of condensed matter physics will then affect virtually every discipline in the physical sciences, life sciences, and engineering. The goal of this proposed research is twofold: (1) develop new conceptual tools to advance the knowledge of strong correlations in non-equilibrium settings and (2) study many-body quantum dynamics in realistic experimental situations.

DOE National Laboratories

Exploratory Development of Theoretical Methods

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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$764,000

The scope of this FWP is to generate new theories, models, and algorithms that will be beneficial to the research program at Ames Laboratory and to the mission of DOE. The need to make quantitative theoretical predictions and to obtain detailed agreement between theory and experiment are crucial for the design, characterization and control of complex materials. To stay competitive with the rapid development of advanced theoretical and computational tools, there is an urgent need to invest time and effort in the exploratory development of theoretical methods. This FWP will focus on 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 with the common link only existing in the mathematical formulation of the problem. Such leaps across topic areas, and in some cases across disciplines, are characteristic of the power of a fundamental physics-based approach facilitated by the availability of general theoretical tools applicable to very different sets of problems. Maintaining strength in this FWP will also allow the Ames Laboratory program the capability of agile response to new scientific questions. Currently, this FWP supports work in (a) methods for accurate calculation of strongly correlated electron systems which includes the development of Gutzwiller density functional theory and self-consistent all-electron full-potential GW method; (b) methods for computational prediction and design of complex structures and materials which consists of developments of efficient computational algorithms for exploring configuration space (e.g., genetic algorithm) and accurate interatomic potentials for fast energetic evaluation and large scale atomistic simulation (e.g., tight-binding); and (c) methods for studying the dynamics of non-equilibrium or nonlinear systems including quantum control of electron and nuclear spins in nanosystems and first-principles calculation of spin dynamics and magnetic fluctuation in solids.

FY10 CMSN: Computational Design of Fe-based Superconductors

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Students:	0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$50,000

The purpose of this FWP is to develop a novel approach to tackle the lack of reliable first principle calculations in strongly correlated materials. The theoretical foundations to tackle this problem are based on a non-perturbative many-body method based on a combination of dynamical mean field and Green's function effective interaction (GW) theories, which can yield material-specific predictions and interpretation of properties of solids. Our objectives are to (a) implement this approach using the high-performance, all-electron, full-potential, relativistic linear augmented plane wave method; (b) make major peed-ups to handle Green functions, self-energies, and polarization operators on the frequency and imaginary time axis by introducing novel algorithms and data structures, as well as implementing parallelization technologies at the petascale, which will enable the treatment of complicated systems with many atoms per unit cell; and (c) to apply this powerful many-body tool by tackling frontier problems of materials science, such as computational design of novel iron-based superconductors, to study their photoemission spectra, optical conductivities, total energies, superconductive spectral functions and pairing interactions.

Metamaterials

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Students:	4 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$487,000

Metamaterials are composite materials with novel and unique electromagnetic (EM) properties, which are not determined by the fundamental physical properties of their constituents but by the shape and the distribution of specific patterned inclusions. The scope of the program is the theoretical understanding, analysis, development and testing of metamaterials, particularly left-handed materials (LHMs) and also the investigation of their feasibility for potential applications, that will be beneficial to the research program at Ames Laboratory and to the mission of DOE. Maintaining strength in this FWP will also allow this Ames Laboratory program the capability of agile response to new scientific questions.

Nanoscale and Ultrafast Correlations and Excitations in Magnetic Materials

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Students:	3 Postdoctoral Fellow(s), 5 Graduate(s), 2 Undergraduate(s)
Funding:	$1,078,000

Magnetism is a traditional subject, yet one with modern branches experiencing great vitality. One new branch features magnetic materials with nano dimensions exhibiting behavior not encountered in bulk samples. In this FWP the emphasis is on using precise and accurate theoretical and experimental techniques to investigate, understand, and control aspects of magnetic materials where nanometer size dimensions are of importance. Such materials include zero-, one- and two-dimensional magnetic systems (i.e., quantum dots or isolated magnetic molecules, 1-D chains, and 2-D layers or islands). We seek to answer fundamental questions such as how do itinerant characteristics and extended excitations emerge with size? How are magnetic interactions and excitations in magnetic molecules, quantum dots and islands, chains, and layers affected by edges, lines, and different surface substrates? Can we dynamically control the magnetic moment, electronic transport, and optical response by optically pumping selected electronic states? A key approach to these questions is the growth of single crystals of the above magnetic systems with various dimensionalities. Using neutron and x-ray scattering measurements, the exact positions of the atoms are determined, and the emergence of complex magnetic behavior is precisely measured. Accurate theoretical models for these systems are developed. Experimental facilities probe spin interactions (often to milliKelvin temperatures) by NMR, fast optics, highly precise magnetic susceptibility, magnetic x-ray and neutron scattering and magnetic STM techniques. A new approach is to grow uniform (a few atoms in height) magnetic islands on non-reactive substrates exploiting electron confinement. This work has implications for quantum dot devices in spintronics, magnetic recording, ultrafast switches, and qubit technology for quantum computing. The overall goal is to identify clean, prototypical nanoscale model systems where the magnetism can be thoroughly understood experimentally and theoretically, and then to transfer that knowledge to improve or foster applications.

Condensed Matter Theory

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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,600,000

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.

Quantum Mesoscopic Materials and Structures

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$780,000

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 graphene with partially ordered adatoms. In the initial stage we performed an intensive theoretical analysis of the properties of metamaterials, based on recent breakthroughs in quantum condensed matter theory, such as many-body localization, discovery of the superinsulating state, and the theory of transport in granular materials. In particular, we constructed a theory of gigantic jumps in the electric currents near the superconductor-insulator transition and outlined a theory of cascade relaxation governing tunneling transport in non-standard insulators.

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, 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.

Theory Institute

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Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $250,000

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. MTI implements its goals through an intensive visiting program, which brings top experts, both distinguished scientists and outstanding young talents, to work on high impact problems and emerging topics and themes in materials theory, and to bring new revolutionary science to MSD. The topics to be pursued and the respective visitors are selected by an internal Scientific Advisory Committee from competitive proposals solicited from all MSD staff and also from the outside researchers. MTI also identifies top early career and established theorists as candidates for recruitment to postdoctoral and permanent positions at Argonne. MTI holds a series of the topical fall workshops on the most urgent subjects related to existing MSD projects which promise to stimulate new research directions at MSD. During the past three years MTI succeeded in reaching world leading research groups that resulted in the discovery of the superinsulating state and outlining theories of electronic and thermoelectric effects in granular and disordered strongly correlated materials, and held an International Workshop on the Superconductor-Insulator transition. We plan to continue pursuing cutting edge research directions and contribute to sponsoring topical workshops.

CMSN

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Johnson, Duane, AMES LABORATORY
Shelton, William, PACIFIC NORTHWEST NATIONAL LABORATORY
Students: 3 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $220,000

The program enables collaborations between PIs of different institutes to address difficult and timely scientific issues concerning the physical roles of impurities and short-range correlations in functional materials. The main emphasis of our CMCSN team consists of new computational methods for disordered systems, and applications to functional materials of practical importance. By design, the CMCSN funding is to provide leverage to the existing funding of the PIs by supplying travel support and inter-institute “seed” projects.

Scientifically, the exchange of technology was implemented through the extended visits of students. In addition, two new computational methods were developed. A dual fermion formulation of the multi-scale method is conducted and is now being implemented. On the other hand, first-principles derivation of effective influence of impurities is developed and tested for real materials. Combining these two capabilities, the team is now proceeding to the development of dynamical cluster approximation using the first-principles derivation. In addition, applying existing methods developed by the team members, studies of doping and substitution of Fe-based superconductors were performed. Specifically, a study on whether transition metal substitution of Fe dopes the system is performed. It was found that while the charge difference appears to be localized, the corresponding electronic structure in fact resembles that of highly doped systems. Interestingly, strong loss of coherent spectral weight and development of incoherent features are found, which can modify significantly the competition between magnetism and superconductivity.

Condensed Mattery Theory

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Sr. Investigator(s):	Konik, Robert, BROOKHAVEN NATIONAL LABORATORY Ku, Wei, BROOKHAVEN NATIONAL LABORATORY
Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,450,000

In FY2011, as part of this FWP, the following projects have been worked on: (1) magnetic systems (A. Tsvelik and Wei Ku in collaboration with the X-ray experimental group at BNL and the Neutron Scattering Group), (2) nanosystems (R. M. Konik), and (3) non-equilibrium one-dimensional systems (R. M. Konik).

The magnetic systems of interest include transition metal oxides (TMO) and frustrated magnets such as pyrochlores. The strong spin-orbit coupling present in TMO generates highly anisotropic exchange interactions opening a possibility of realization in these systems of the famous Kitaev model widely believed to be a fundamental model for a quantum computer. An alternative realization of such a model based on quasi-one-dimensional materials with a ladder-like structure was recently suggested by A. Nersesyan and A. Tsvelik (EPL, 96, 17002, 2011).

The research in nanosystems has been based, in part, on the new numerical approach developed by R. M. Konik. The application of this approach to the model of semiconducting carbon nanotubes with unscreened Coulomb interaction yielded a theoretical prediction (PRL, 106, 136805, 2011) for the excitonic spectrum in good agreement with experimental observations conducted by BNL’s Misewich and Sfeir group.

In work on non-equilibrium one-dimensional systems, using the same numerical approach as above, R.M. Konik has been exploring quantum quenches in atomic Bose gases and in quantum spin systems such as the quantum Ising model. This work has been done in conjuction with J.S. Caux (U. van Amsterdam) and G. Mussardo (SISSA, Trieste).

Electronic Properties of Transition-Metal-Compound Nanotubes

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Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$410,000

A novel first-principles Wannier function based method for disordered materials was developed, which enabled studies of physical effects of disordered impurities in real materials. Unlike the state-of-the-art computation methods, this beyond-mean-field method allows scattering processes involving multiple impurities, and thus for the first time produces weakly localized states of large size within first-principles calculations. Applying this new capability to the highly debated issue concerning the hole pockets in sodium intercalated cobaltates revealed that the disordered sodium intercalants cannot destroy the hole pockets as previously proposed. In fact, the pockets turn out to be one of the least affected features by disordered sodium intercalants. The same method is also applied to the study of oxygen vacancies and Cu substitutions of ZnO, a room temperature ferromagnetic semiconductor. Our results provided important information that the oxygen vacancy states lie higher in energy than the upper Hubbard band of the Cu impurities. Consequently, the popular idea of magnetic polaron mechanism is not applicable. An alternative picture was then proposed in the same study to explain the microscopic processes that lead to the ferromagnetism and explain the soft X-ray circular dichroism.

In FY2011, this program produced seven publications: 1 PRX, 2 PRL, 3 PRB and 1 JACS, with emphasis on studies of electronic structure of Fe-based high-temperature superconductors and strong spin-orbit coupled Ir compounds. In addition, a generic theory for superconducting gap was formulated for underdoped cuprates within the strong coupling limit. The theory was shown to describe the superconducting gap in absolute scale without any free parameter.

Carrier Dynamics in Heterostructure Nanosystems

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Students:	0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$120,000

In many nanostructure applications the carrier dynamics assisted by electron-phonon interaction plays a critical role. In a heterostructure nanocrystal solar cell, it will be important to know where does the hot carrier spatially relaxed to after initial excitation, and whether they can be collected directly by the electrodes (instead of forming excitons). This cooling mechanism can be combined with electron-hole Coulomb interactions, e.g., to overcome the phonon bottleneck, or to possibly generate multiple excitons. In a heterojunction solar cell, the carrier transfer between different parts of the structure is often the bottleneck of the overall efficiency. The nonradiative carrier decay is related to multiple phonon assisted carrier trapping. Previous treatments of phonon assisted carrier transport often involve analytical approximations derived from bulk systems. We will tackle these problems numerically with high fidelity ab initio calculations. We plan to study the incoherent carrier transport via electron-phonon couplings in nanocrystals, as well as the coherence elastic quantum transports in device simulations. We will also test the use of time domain method to simulate the carrier dynamics which treat coherence and incoherent carrier transport in a single framework.

Charge Patching Method for Electronic Structures and Charge Transport of Organic and Organic/Inorganic Mixed Nanostructures

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Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $275,000

The goal of this project is to develop new methods to study the electronic structures, optical properties and charge transports of large organic molecules, and organic/inorganic mixture systems. This will extend our capability of calculating such systems from a few hundred atoms to hundreds of thousands of atoms in ab initio quality. The methodology developments include the charge patching method, the linearly scaling divide-and-conquer method, the fragment based method, carrier transport methods, as well as new computational algorithms. The physics to be studied include organic/inorganic interface, disordered organic systems, density of state, state localization, electron-phonon interaction, and carrier hopping in organic and organic/inorganic mixed systems. Disordered organic systems, nanocrystals, and organic/inorganic mixed systems have been used for many different electronic and optical applications. But conventional ab initio calculations cannot be used to study them due to their large sizes. This makes the methodology development necessary. Such capability also allows us to study new phenomena pertinent to such systems, like the electron-phonon interaction, and the carrier hopping transport.

Theory and Simulation of Defects in Oxides

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Sr. Investigator(s):
Students: 3 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $115,000

Theoretical calculations and simulations are carried out for oxide materials. Our focus is on the nature of defects in oxides, with a particular emphasis on transition metal oxides. Many of these materials serve a crucial role in modern electronics, information materials and energy materials. The effort here at LBNL is part of a multi-institution TMS program with the University of Texas at Austin as the lead institution. The team consists of researchers with expertise in device physics, chemical engineering, materials science, materials physics, computational physics, numerical analysis and computer science. State of the art computational approaches and theory will be developed and used.

Theory of Materials

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Funding: $334,000

This is a broad-based program to understand and compute material properties and behaviors involving three principal investigators and covering two complementary efforts: (1) quantum theory of materials and (2) strongly correlated electron systems. Novel materials and new concepts are explored. A variety of theoretical techniques are employed, ranging from first-principles electronic structure calculations to new conceptual and computational frameworks suitable for complex materials/nanostructures and strongly interacting electron systems. One emphasis is to investigate realistic systems employing microscopic first-principles approaches. Model systems are also examined. Studies include bulk materials, nanostructures, superconductors, surfaces and interfaces, and reduced-dimensional systems. Close collaboration with experimentalists is maintained. Another emphasis is to push the frontier of theory beyond the Landau paradigm toward a framework capable of describing and predicting the behavior of strongly correlated systems. Through interaction with experiment, new phases, new phase transitions, and new organization principles may be discovered. Equally important is the development of computational methods suitable for increasingly complex materials and strongly correlated materials.

The Theory of Materials program additionally received at least half of the research effort of three postdoctoral fellows and four graduate students who were supported by outside sources (fellowship, TAship, etc).

Accelerated Molecular Dynamics Methods

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Funding: $310,000

Molecular dynamics (MD) simulation, a powerful tool for probing systems in full atomistic detail, is limited to a few microseconds or less, while many activated processes in materials take place on much longer time scales. Moreover, most real systems have a complexity that makes it difficult or impossible to accurately predict their dynamical evolution using intuition or simple models. Accelerated molecular dynamics methods, developed over the last dozen years at Los Alamos, offer a way out of this dilemma. Built on solid statistical mechanical concepts, these methods follow the long-time evolution of activated processes in full, accurate detail. Simulations so far on processes such as surface diffusion and growth, bulk diffusion, radiation damage annealing, and grain-boundary sliding and nanoscale kinetics show the methods are extremely powerful. We can reach time scales of ms, s, and beyond, and we invariably observe complex, unanticipated behavior, even in situations where the dynamics were expected to be simple. We are now applying the methods to assist other DOE programs at LANL, and developing the methods further to overcome key obstacles, with the goal of making them applicable to the widest possible range of problems. In particular, we are developing new algorithms for getting around the low-barrier problem, treating more complex systems, and making use of massive parallelism. We are developing user-friendly software and collaborating on applications with experts from around the world. Feedback from the collaborations in turn shows us where further development is most needed.

Integrated Modeling of Novel Materials

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Funding:	$380,000

Complex electronic materials are of great scientific interest. These materials exhibit strong electronic correlations along with strong electronic coupling to multiple degrees of freedom, like lattice and spin. New tools, such as the Scanning Tunneling Microscope (STM) and the Atomic Force Microscope (AFM) were applied to these materials. They reveal substantial spatial inhomogeneity in high-Tc cuprates and manganites and possibly in heavy fermion materials. Electronic inhomogeneity in these materials appears to be a more common occurrence than we thought earlier. Theoretical understanding of the role of inhomogeneity, coupling to spin and lattice degrees of freedom and competition between different phases in these materials is a crucial missing step in our understanding of these materials. The overarching goal of the project is to provide an understanding of the fundamental physical processes that determine nanoscale inhomogeneity and coupling between various degrees of freedom in correlated electronic materials. Physical processes of interest include drivers and mechanisms of inhomogeneity, coupling to local lattice and spin degrees of freedom, transport, and dynamics. Our goals are to discover new laws that govern the behaviour of states of matter and to create the essential new understanding and interpretative framework demanded by these discoveries. We will further develop numerical and analytic methods that will make possible detailed analysis and predictions about specific experimental properties. Ultimately we would like to use the theoretical understanding developed in this work to predict and develop new functionalities in these materials.

Semiconductor Theory

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Luo, Jun Wei, NATIONAL RENEWABLE ENERGY LABORATORY
Zunger, Alex, NATIONAL RENEWABLE ENERGY LABORATORY
d'Avezac de Castera, Mayeul, NATIONAL RENEWABLE ENERGY LABORATORY
Students: 5 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $450,000

This “Semiconductor Theory” project aims to create the fundamental solid-state physics underpinning of the energy-related semiconductor and nanostructure systems using state-of-the-art tools of condensed matter theory. This will create a fundamental understanding of basic mechanisms underlying the building blocks of energy conversion. The central purpose of the current FWP proposed work focuses on forging an understanding of the relationships between atomic microstructure (e.g., clustering, phase separation, partial order, nanostructure formation) and its ensuing electronic structure (e.g., localization, multiple-exciton generation, charge separation). We aim to “bridge the gap” between the (a) theory of atomic microstructure and (b) theory of electronic properties (optical, electrical) ensuing from such microstructures.

Theoretical Studies of Complex Collective Phenomena

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Fishman, Randy, OAK RIDGE NATIONAL LABORATORY
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Moreo, Adriana, TENNESSEE, UNIVERSITY OF
Students: 0 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding: $1,734,000

The overarching goal is to understand the emergence of complex collective phenomena in a variety of materials, including strongly correlated electrons in bulk compounds and nanostructures, mainly using model Hamiltonians and non-perturbative theoretical techniques. The scientific effort is focused on (1) analysis of novel bulk magnetic and superconducting phases, where phenomena such as high-temperature superconductivity, colossal magneto-resistance, magnetism in organic compounds, multiferroicity, and self-organization into inhomogeneous nanoscale patterns is addressed; (2) study of artificially created nanostructures, involving oxide and magnetic multi-layers, with emphasis on the phenomenon of electronic and orbital reconstruction at surfaces and interfaces, and on the prediction of novel functionalities; and (3) development of quantum Monte Carlo techniques for ab-initio studies of correlated electronic systems. Our goals are related to experimental efforts in the BES program at ORNL, including programs such as Scanning Transmission Electron Microscopy (ERCKS89) and Interfaces in Complex Oxides (ERKCS80). Our research relates to energy issues via our study of high temperature superconductors, and oxide interfaces employing magnetic and multiferroic materials, with the potential for sensors, actuators, as well as energy storage and conversion approaches.

Theoretical Studies of the Formation, Stability and Properties of Low Dimensional Materials

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Xiao, Di, OAK RIDGE NATIONAL LABORATORY
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Zhu, Wenguang, TENNESSEE, UNIVERSITY OF
Gao, Yanfei, TENNESSEE, UNIVERSITY OF
Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $1,167,000

State-of-the-art theoretical approaches are used to advance the scientific understanding of the formation, stability, and properties of low-dimensional materials and, through synergy with experiment, to aid the design and discovery of novel 0-, 1-, and 2-dimensional systems where emergent and optimized properties may be found. Emphasis is placed on the control and manipulation of growth mechanisms and prediction of structural, optical, magnetic, chemical, and transport properties. Examples include the following:

- first principles studies of the structure, dynamics, and statistical physics of magnetic nanostructures
- development of ab initio approaches to the theory of finite temperature properties of magnetic materials and nanostructures based on combining Wang-Landau sampling with first principles DFT electronic structure methods
- theory of topological insulators
- nanomechanics of defects and interfaces and their effects in structural and functional properties of low-dimensional materials
- tuning of stability, growth, and microstructural evolution of nanoscale thin-film heterostructures
- optical and plasmonic properties of low dimensional materials
- understanding and controlling novel spintronic interactions and magnetolelectric effects in multifunctional materials

Theory of Complex Materials

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Samolyuk, German, OAK RIDGE NATIONAL LABORATORY
Stoller, Roger, OAK RIDGE NATIONAL LABORATORY
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Funding: $1,402,000

The overarching goal is to use state-of-the-art theory to advance understanding of complex materials. The emphasis is on atomic level understanding of materials properties within the rich backdrop provided by ORNL experimental efforts. Theory impacts the program through interpretation of results, prediction of materials with enhanced properties, and definition of critical experiments. We identify the underpinnings of structural and mechanical properties of advanced alloys and intermetallics. This is leading to understanding of long-standing problems, including the chemical bonding of novel high pressure phases, and development of accurate metal-H/He potentials for predictive molecular dynamics studies of defect/dislocation interactions. We use first principles and first principles-based theories to unravel chemical and structural underpinnings of properties, including magnetism, ferroelectricity, and transport. Particular emphasis is on elucidating the fundamental origins of complex behavior observed in novel materials under experimental investigation at ORNL. This work directly relates to the needs for better radiation tolerant materials to enable new generations of safe nuclear reactors, high temperature materials for critical components of high efficiency engines, e.g., exhaust valves, and turbo-machinery for power generation and aviation, dielectric energy storage for regenerative braking, piezoelectric fuel injectors for automotive clean diesel, and advanced rare earth free magnets for wind generation and electric vehicles.

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: $150,000

Understanding how novel behavior emerges in complex materials as a consequence of competition and interactions between microscopic degrees of freedom is a key challenge in condensed matter. Given the dynamical nature of these interactions, ultrafast optical spectroscopy has a great deal to offer as it provides the ability to temporally resolve phenomena at the fundamental timescales of atomic and electronic motion. The goal of this research program is to investigate the role of the spin, charge, lattice, and orbital degrees of freedom in determining the fundamental physical properties of complex materials using ultrafast optical spectroscopy.

The majority of our effort will focus on dynamics in transition metal oxides (TMOs) of contemporary interest specifically including the following:

(a) V_2O_3 is perhaps the most canonical of the TMO in terms of metal-insulator physics. In V_2O_3 we will investigate the possibility of photoinduced phase transitions starting from the antiferromagnetic insulating state and the correlated paramagnetic metallic state.

(b) Pr0.7Ca0.3MnO_3 is a charge ordered manganite that is precipitously close to metallicity such that it is susceptible to optical perturbations. In the charge ordered state a collective charge density wave mode manifests at THz frequencies which will serve as a probe of the degree to which the charge order has "melted" following photoexcitation.

(c) $BiFeO_3$ is a multiferroic whose interactions can be strain engineered through controlled epitaxial growth. $BiFeO_3$ exhibits interesting optical and far-infrared properties whose dynamical origin is not fully understood. Multipulse terahertz emission spectroscopy will allow us to gain insights into the nature of the picosecond ferroelectric depolarization dynamics.

We will also initiate an exploratory effort where we integrate plasmonic or metamaterial structures with TMOs. The goal is to utilize the electromagnetic field enhancement of such structures to accentuate the "photosusceptibility" of TMOs potentially resulting in, as but one example, a reduced fluence threshold to photoinduce a phase transition.

Real-time X-ray Studies of Surface Structure Evolution in a Plasma Environment

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$116,000

Better understanding of complex surface and thin film processes continues to be an important materials science challenge. We are investigating fundamental issues in thin film growth and interface structure using real-time x-ray studies. These experiments take advantage of a facility we have co-developed at the National Synchrotron Light Source (NSLS) insertion-device beamline X21. It enables a wide array of x-ray techniques to be employed, including grazing-incidence diffraction, grazing-incidence small-angle scattering, reflectivity, fluorescence and x-ray absorption edge spectroscopy.

Recent work has largely focused on examining the fundamental kinetics of thin film growth by island formation, impingement and coalescence, particularly in films of Ga and In and their nitrides. Both GaN and InN have significant applications in optoelectronic, solid-state lighting and photovoltaic devices and we have found that epitaxial nanodots can be grown by plasma nitridation of nanodroplets. However a primary focus of our research has been on developing a more complete understanding of the fundamental kinetics of droplet formation and coarsening in these materials. The classic theory/simulation work in the field, from Family and Meakin [Phys. Rev. A 40, 3836 (1989)], neglects the effects of surface diffusion by adatoms. Our own data shows that surface diffusion plays a major role for Ga and In droplets on GaN and sapphire substrates at elevated temperatures. We are using simulations and comparing their predictions to experimental data to better understand the surface kinetics.

To examine how the ideas of liquid droplet formation and growth can be generalized to solid thin film growth by island formation and coalescence, we have taken synchrotron data on the room-temperature growth of Al islands by deposition from an effusion cell. Interestingly, the kinetics of island formation is surprisingly similar to that previously observed for liquid droplet formation. A key difference is that, at this temperature, there is no diffusion between islands, and hence no island coarsening in the absence of deposition. Moreover, the x-ray scattering amplitude from the growing islands during deposition grows more slowly than predicted by the Family-Meakin model. We believe that this is likely due to the finite rate of island coalescence when they impinge – in the Family-Meakin model of liquid droplets, coalescence is instantaneous. Our simulations are in general agreement with this supposition.

To broaden our understanding, we are also examining how the results from droplet/island evolution can be used to better understand the early stages of the MBE growth of InN solid thin films.

Optoacoustic Microscopy for Investigation of Material Nanostructures - Embracing the Ultrasmall, Ultrafast, and the Invisible

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Sr. Investigator(s):	
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Funding:	$200,000

This proposal targets the development of a new type of scanning acoustic microscope for nanometer resolution ultrasound imaging, based on ultrafast optoacoustics. In the microscope, subpicosecond laser pulses will be used to generate and detect very high frequency ultrasound with nanometer wavelengths. We propose to design and construct an instrument that can be used for quantitative imaging of nanoscale material features – including features that may be buried so as to be inaccessible to conventional lightwave or electron microscopies. The proposed research program aims to produce a prototype scanning optoacoustic microscope which, in combination with advanced computational modeling, will be applied for specific material nanostructures, particularly those that are of contemporary interest to the frontline micro- and optoelectronics device industry. A broader goal of the research is to develop the optoacoustic microscope to make it a user tool that will be available for a wide range of applications and innovations for tomorrow‘s material science and precision metrology.

Nanoscale X-Ray Imaging and Dynamics of Electronic and Magnetic Materials

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Funding:	$170,000

The emergence of nanoscale or mesoscale correlated electronic and magnetic phases, phase transitions, self-organization and nanoscale phase separation is at the heart of many fundamentally experimental condensed matter systems. However, it has been difficult to quantify the emergence of electronically or magnetically ordered domains and capture their structural and dynamical behavior, due primarily to the lack of spatio-temporal probes capable of directly coupling to the structure and dynamics of relevant bulk order parameters at nanometer lengthscales.

The objective of this proposal is the development and application of novel experimental approaches based primarily on x-ray scattering techniques using the unprecedented brightness of 3rd and 4th generation synchrotron source facilities. In particular, we will develop and apply the Scanning X-ray Nano-diffraction, as well as coherent x-ray scattering techniques, such as Coherent X-ray Diffractive Imaging and X-ray Photon Correlation Spectroscopy.

These techniques will become crucially important tools in exploiting the nanoscale physics of electronic and magnetic structures in correlated materials – such as colossal magnetoresistive manganites or metal-insulator transition in vanadites, sliding charge density waves, spin density wave domains in quantum magnets, nanoscale magnetic domains in transition metal and rare earth magnetic thin films and multilayers. We propose addressing the physics of these systems with a suite of novel coherent and nanodiffraction x-ray techniques which combine imaging and scattering approaches.

Understanding of fundamental nanoscale physics of electronic materials is a crucial cornerstone for developing ways in which electronic and magnetic order parameters can be designed, controlled and manipulated, producing a new generation of electronic computing, communication and media storage devices with desired functionality at nanometer lengthscales.

HPCAT -- An Integrated High-Pressure Facility at the Advanced Photon Source

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,087,000

The present BES Core Program Grant DE-FG02-99ER45775 provides the key 35% of the total budget support for the High-Pressure Collaborative Access Team (HPCAT) which operated the Sector 16 synchrotron beamline facility at the Advanced Photon Sources of Argonne National Laboratory. HPCAT is dedicated to high-pressure (HP) research in multidisciplinary scientific areas by integration of multiple, x-ray diffraction and spectroscopy probes, as well as complementary non-x-ray probes, with DAC samples under extreme pressure –temperature (P-T) environments. The thriving research at HPCAT has impacted an exceedingly broad scientific frontier. Discoveries in HP physics include pressure-induced superconductivity, ferroelectricity, colossal magnetoresistivity, phonon softening, Fermi-surface nesting, d-electron spin pairing, f-electron delocalization, insulator metallization, etc. Pressure-altered chemistry includes novel nitrides, hydrides, oxides, simple molecular compounds, crystal amorphization, bonding changes, photochemistry, etc. These fundamental discoveries impact on the applied sciences, ranging from understanding the Earth’s and planetary deep interiors to syntheses of novel and useful materials.

A plethora of state-of-the-art high-pressure synchrotron probes have been pioneered and developed at HPCAT to explore the rich physics and chemistry under pressure by the general high-pressure research community. The HP x-ray diffraction techniques at HPCAT yield comprehensive crystallographic, bonding, density, elasticity, deviatoric elastic, rheological, and orientational information of single-crystal, polycrystalline, nanocrystalline, and non-crystalline samples in-situ under HP. The HP x-ray spectroscopy techniques at HPCAT include HP x-ray emission spectroscopy which provides information on the filled electronic states of the HP samples, HP x-ray Raman spectroscopy which reveals pressure-induced chemical bonding changes of the light elements, HP inelastic x-ray scattering spectroscopy which accesses the high-energy electronic phenomena, including electronic band structure, Fermi surface, excitons, plasmons, and their dispersions. The HP x-ray spectroscopy techniques also include HP resonant inelastic x-ray scattering spectroscopy which probes shallow core excitations, multiplet structures, and spin-resolved electronic structure, and HP nuclear resonant x-ray spectroscopy which provides phonon densities of state and time-resolved Mössbauer information. These tools, newly integrated with hydrostatic or uniaxial compression, laser heating, and cryogenic cooling, have enabled users' investigations of HP structural, vibrational, electronic, and magnetic properties that were unimaginable only a decade ago.

The extraordinarily impact of HPCAT is manifested in many ways. HPCAT is the nation's leading synchrotron users facility for the broad high-pressure community including universities government, and private research organizations. HPCAT serves as an important resource for education; dozens of Ph.D. and M.S. theses have been based in part on research conducted at HPCAT. The basic scientific research at HPCAT has consistently produced over 75 publications per year in the open literature, of which over 20% appeared in "high-profile" journals with "Impact Factors" greater than 7, that is a record second to none among physical science synchrotron beamlines in the world.

Magnetic and Superconducting Materials at High Pressures

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

Research on the behavior of materials at high pressures is expanding dramatically. As a result of developments in diamond-cell technique a broad range of studies of the physical and chemical properties of solids can be now conducted in-situ at high pressures to several hundred gigapascals. When pressure is increased on solids, interactions between atoms increase, in some cases radically altering a material's physical and chemical properties. In contrast, changing interatomic distances by varying composition is restricted by the discrete nature of chemical elements, and tuning by temperature is complicated by thermal excitations (i.e., vibrations) and ultimately the melting and boiling points of the material. Thus, the application of pressure provides an ideal means to carefully tune electronic, magnetic, structural and vibrational properties for a wide range of applications.

Scientific goals of the project consist of identifying and characterizing magnetic and superconducting properties of transition metals and their oxides, and investigating new classes of superconductors. These can be itemized as follows: (1) exploring new potential elemental superconductors (hydrogen, alkali metals) and already known superconductors at the limit of static high pressure techniques; (2) investigating special classes of superconducting compounds (hydrides, high-Tc superconductors, borides, carbides, nitrides) 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, magnetic/phase transformations, and electronic structure in transition metals, and transition metal materials, including transitions from ferromagnetic to nonmagnetic phases in a broad pressure-temperature range; (4) advancing synchrotron spectroscopy, transport, and magnetic techniques for measurements on small samples at very high pressures in a wide temperature range.

Exploration of the pressure variable is increasing the number of known materials. Because of pressure-induced changes in chemical affinities, the reactivities of otherwise familiar elements and compounds are totally altered, and entirely new classes of materials are appearing. Very precise pressure tuning allows observation of the details of the pressure-induced insulator-metal transition and even more subtle changes in the electronic structure, thus expanding the horizon in the search for novel physical phenomena at ultrahigh pressures.

Quantifying Damage Accumulation During Ductile Plastic Deformation Using Synchrotron Radiation

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Funding:	$400,000

Polycrystalline materials play key roles in infrastructure systems that serve in hospitable and extreme environments in energy, transportation and many other sectors of the economy (bridges, car frames, nuclear reactor cores, propulsion and power turbines, and fuel cells, to name a few). Application critical macroscopic properties emerge from nano-scopic and meso-scopic features such as crystalline grain sizes and relative orientations, grain boundary types, defect content and stress states. The considerable understanding of processes such as material failure has been developed through destructive testing: breaking the material open to see what happened and correlating statistics from differently prepared samples. Recently, however, it has become possible, using synchrotron based High Energy X-ray Diffraction Microscopy, to non-destructively measure the positions, shapes, and crystallographic orientations of grains deep inside of materials and to localize strain measurements to individual grains. High energy x-ray tomographic measurements have detected internal voids as they nucleate and grow deep inside of bulk samples.

Our research uses a combination of recently developed experimental techniques, primarily at Argonne National Laboratory's Advanced Photon Source beamline 1-ID, to observe the process of void nucleation and growth in metals as they undergo deformation. We seek to locate void positions and growth habits relative to microstructural features such as quadruple points, triple lines, and grain boundaries. Combined x-ray tomography and microstructure mapping follows the evolution of samples in three dimensions as macroscopic strain is applied. Initial work is concentrated on two simple model materials, copper and zirconium. Copper is a soft, ductile material with cubic crystal structure while zirconium is stiffer and has a hexagonal crystal structure which generates more complex anisotropic behavior.

The impact of the experimental measurements is extended through computational modeling using the measured microstructures as input. A relatively new fast Fourier transform (FFT) based method is used that permits the visco-plastic stress-strain response of polycrystals to be calculated from a direct image of the microstructure. Models will be constrained through direct comparison to experimentally observed evolution. This type of comprehensive study of a small number of model systems 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. Data sets will be made available to the materials community so as to optimize their impact. Furthermore, the methodologies and experimental capabilities developed within the project are directly generalizable to other materials of practical interest.

Ultrafast Magnetism Dynamics Measure Using Tabletop Ultrafast EUV Sources

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Funding:	$260,000

The underlying physics of all ferromagnetic behavior is the cooperative interaction between individual atomic magnetic moments that results in a macroscopic magnetization. However, magnetism at nanometer scale lengths on ultrafast timescales is not well understood either theoretically or experimentally, since no complete microscopic model of how spins, electrons, photons and phonons interact currently exists. Moreover, this topic is also directly relevant to nanotechnology, since individual bits stored on a hard disk are already of sub-20nm dimension, and advances in storage capacity and energy efficiency depend on further increases in magnetic switching speed and storage density. Until recently, magnetic material dynamics used either ultrafast visible-wavelength lasers or x-rays from large-scale synchrotrons; the former gives short pulses (~ 50 fs), enabling studies in the ultrafast regime but with low spatial resolution and without element-specificity. X-rays give high spatial resolution and high contrast at the elemental absorption edges of the ferromagnetic materials; however, until recently the time resolution is too low to capture the fastest coupled dynamics involved in magnetism. In recent work, we used extreme ultraviolet pulses from high-harmonic generation as an element-specific probe of ultrafast, optically driven, demagnetization in a ferromagnetic Fe-Ni alloy (Permalloy). We uncovered that for times shorter than the characteristic timescale for exchange coupling, the magnetization of Fe quenches more strongly than that of Ni. Then as the Fe moments start to randomize, the strong ferromagnetic exchange interaction induces further demagnetization in Ni, with a characteristic delay determined by the strength of the exchange interaction. We further enhanced this delay by lowering the exchange energy by diluting the Permalloy with Cu. This measurement probes how the fundamental quantum mechanical exchange coupling between Fe and Ni in magnetic materials influences magnetic switching dynamics in ferromagnetic materials relevant to next-generation data storage technologies.

Influence of Pressure on Physical Property of Ammonia Borane and its Re-Hydrogenation

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We have investigated phase stability of ammonia borane at high pressures up to 11 GPa (with an interval of 0.35 GPa) and elevated temperature up to 80°C using diamond anvil cell (DAC). In-situ Raman spectroscopy shows that most of the phase transitions shift towards lower pressure with increasing temperature. However, pressure for the phase transition at ~0.9 GPa and ~10.2 GPa does not change with temperature. From 40°C to 80°C, we found a new Raman peak splitting at about 6 GPa which is not observed at room temperature. The effect of pressure on the tetragonal to orthorhombic phase transition at low temperature was also investigated in diamond anvil cell. The temperature of the disordered tetragonal to the ordered orthorhombic phase transition increases with applied pressure, which indicates pressure enhances the ordering of the structure. The Clapeyron slope of the transition was determined to be dP/dT = 25.7 MPa/K, indicating the transformation is of exothermic. Pressure does not have any effect on the required undercooling for the appearance of all the Raman modes characteristic of orthorhombic phase.

Upon future cooling down to 90K in the pressure range up to 14 GPa, four new phases were discovered through changes in characteristic Raman spectra. Throughout the whole pressure region, both the symmetric and asymmetric NH stretching modes show red shift with pressure, which indicates the weakening of N-H bond. This behavior indicates the presence of dihydrogen bonding in this material. On the other hand, the BH symmetric and asymmetric modes show blue shift with pressure, which indicates the strengthening of B-H bond. New phases appear when temperature decrease below 200K. At pressures between 1 and 5 GPa, the intense asymmetric B-H stretching mode splits into two peaks and a new peak appears near the asymmetric BH_3 deformation mode as temperature decreases. In addition four sharp lattice modes appear which indicates significant ordering of this new phase (A) compared to the tetragonal phase. At pressures between 5 and 7 GPa, the asymmetric BH stretching double splits into four modes and the symmetric BH_3 deformation mode disappears as temperature decreases. In addition, the high frequency NBH rocking mode splits into three modes and two additional new lattice modes appear along with the lattice mode I becoming more intense, which indicates the structure of this new low temperature phase (B) is also more ordered. At pressure between 7 and 11 GPa, the BH asymmetric doublet merges into singlet and a shoulder peak appears for the asymmetric NH stretching mode as temperature decreases. In addition, a new peak appears between the doublet of the asymmetric BH_3 deformation mode while NH_3 deformation doublet merges into singlet (New phase C). At pressure above 11 GPa, the BH asymmetric singlet which is characteristic of the ambient temperature phase starts to split into two modes as temperature decreases. The unassigned overtone mode at ~1560 cm-1 for the ambient temperature phase also splits into two modes; a new peak appears at BH3 asymmetric deformation doublet. High frequency NBH rocking mode splits into multiple modes while the low frequency NBH rocking mode splits into two modes (New phase D).

In-situ x-ray diffraction patterns on both ammonia borane and lithium amidoborane have been collected at high pressures. Further investigations are under way.

Quantum Physics of Surface-Based Nanoscale Systems

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Funding:	$473,000

Understanding the physics and chemistry of surfaces, interfaces, and tailored structures is critical to a wide range of scientific and technological issues, particularly as we look towards the nanoscale and quantum regime. This research project is a study of the electronic 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, which are sensitive to the physical dimensions and boundary conditions. As a result, the electronic properties of such systems including the wave functions, total energy, electronic charge 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 structures. These effects can be very pronounced at the nanoscale because of quantum coherence, which links together the electronic responses of the different parts of the system. Additionally, as the solid-vacuum boundaries are often soft, the atoms and the accompanying electrons may readily morph or diffuse to adopt new metastable or intermediate configurations corresponding to the local minima in a complex multi-dimensional free-energy landscape. These electronically driven transformations are enhanced at elevated temperatures, where fluctuation, entropy, and kinetic effects come into play. The system may undergo atomic reorganization and structural evolution with details that are difficult to predict based on the known bulk behavior alone. These effects and phenomena are of basic importance to nanoscale science and technology, a prevailing national research theme.

This project aims at a fundamental understanding of the underlying physics with a focus on model systems. Our efforts will be directed mainly at three areas of research: (1) in-depth studies of electron-phonon coupling in quantum confined systems and a recently discovered "pseudogap" feature induced by electron-phonon coupling in thin metal films, (2) laterally modulated metal films prepared on stepped Si and Ge surfaces or nanowire-decorated Si and Ge surfaces, and (3) lattice distortion, instability, structural transformation, and lattice dynamics in nanoscale systems. The experimental work, to be carried out at various national and international synchrotron radiation facilities (SRC, APS, ESRF, etc.), will include angle-resolved photoemission measurements of the electronic structure and surface properties, x-ray diffraction measurements of the lattice structure, and x-ray scattering studies of the lattice dynamics and structural transformation. Theoretical calculations and modeling will be performed as needed: simple cases will be handled within the group using standard electronic structure packages or programs developed in-house; more extensive calculations or modeling will be done in collaboration with leading groups.

Resonant Soft X-Ray Scattering Studies of Spontaneous and Engineered Electronic Order in Transition Metal Oxides

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Funding:	$230,000

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. By “instabilities” we refer to spontaneous electronic order such as stripe phases, charge or spin density waves, orbital order, or intrinsic electronic inhomogeneity due to proximity to a quantum critical point. The long-term goal is to understand how these two types of nanoscale order cooperate to create new phenomena, with hopes of contributing eventually to a revolution in strongly correlated electronic devices. This project is based on the technique of 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, with bulk sensitivity.

Some notable achievements supported by this award are the following:

- Demonstration that stripes in high temperature superconductors are charged [P. Abbamonte, et al., Nature Physics **1**, 155 (2005)]
- Demonstration that spin ladders are unstable with respect to the formation of commensurate, Wigner crystals [A. Rusydi, et al., Phys. Rev. Lett. **97**, 016403 (2006)]
- Discovery of an emergent Fermi surface at the interface between $LaMnO_3$ and $SrMnO_3$ [S. Smadici, et al., Phys. Rev. Lett. **99**, 196404 (2007)]
- Discovery of interface charge accumulation at La_2CuO_4-$La_{1.64}Sr_{0.36}CuO_4$ interfaces [S. Smadici, et al., Phys. Rev. Lett. **102**, 107004 (2009)]
- Discovery of a new phase transition in the classic, orbital ordering material $KCuF_3$ [J. C. T. Lee, et al., Nature Physics (published online, Oct. 16, 2011)]

Integral to this activity is pushing the boundaries of what is possible at synchrotron, x-ray light sources. Our group is responsible for the construction and operation of the first dedicated RSXS facility in North America, at beam line X1B at the National Synchrotron Light Source. We are currently constructing a next-generation facility at the Advanced Photon Source, and are planning the world's first high field system at Stanford Synchrotron Radiation Laboratory.

Ultrafast Thermal Transport at Interfaces

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Funding:	$375,000

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 Challange.

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 Challange 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 Challanges 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.

EPITAXIAL OXIDES

Oxide materials within the perovskite family of crystal structures offer a phenomenal variety of physical properties that will enable systematic experiments on the role of interface structure and bonding on ultrafast thermal transport. Oxide thin films will be synthesized by a unique deposition system that combines pulsed-laser deposition, molecular beam epitaxy and real-time monitoring of surface structure by electron diffraction. By placing nanoscale thermometer layers at various distances from a heat source, we will probe interfacial heat transfer on ultrafast time-scales that have not previously been accessible. These thermometer layers will be constructed from perovskite layers engineered to have large temperature dependent changes in optical constants (TDTR and transient absorption), second harmonic generation (TR-SHG), or rotation of optical polarization (TR-MOKE).

NANOPARTICLE/MOLECULAR-LAYER ASSEMBLIES

Interfaces between hard and soft materials will be studied using assemblies of Au nanoparticles and molecular-based thermometer layers. Time-resolved incoherent anti-Stokes Raman scattering (TRIARS) will be enhanced by the plasmon resonance of Au nanorods and will provide state-resolved information about how thermal energy moves between various vibrational states of molecular layers.

Complementary experiments will make use of the optical absorption of spin-crossover molecules as an ultrafast nanoscale thermometer. The separation of the molecular thermometer layers from the nanoparticle surface will be systematically controlled with molecular spacers. In this way, we will probe the physics of heat transfer when the conductance of the interface cannot be treated as a simple boundary condition on the heat diffusion equation.

Optical Manipulation and Detection of Emergent Phenomena in Topological Insulators

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Funding:	$175,000

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.

Ultrafast Electronic and Structural Dynamics in Complex Materials

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Funding:	$175,000

The purpose of this project is to probe the unique collective electronic behaviors of topological insulators by using various time resolved spectroscopic techniques with state-of-the-art temporal and spatial resolution. Topological insulators are recently discovered quantum materials that are insulating in their bulk yet conduct electricity at the surface. Three specific goals of this project are (1) imaging topological spin currents and topological quantum phase transitions using spin sensitive time-and angle resolved photoelectron spectroscopy and time-resolved electron diffraction, (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.

Interfacial Assembly and Chemical Activity of Nanoparticles

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Funding:	$175,000

These studies are designed to elucidate the behavior of nanoparticles at fluid interfaces, including liquid/liquid and molten polymer/molten polymer interfaces. A quantitative understanding of the manner in which NPs assemble at the interface, the dynamics of the NPs in the assemblies, and the kinetics of the assembly process is not fully understood. Here, we propose to characterize the interfacial assembly, the dynamics of nanoparticles assembled at fluid interfaces, the jamming of nanoparticles at fluid interfaces to generate kinetically-trapped morphologies, the formation of micellar structures at these interfaces, and the chemical activity of the NPs by time-averaged x-ray and neutron scattering and reflectivity methods, coherent x-ray scattering, transmission electron microscopy, scanning force microscopy, and laser scanning confocal fluorescence microscopy. In addition, the design and synthesis of functional organic and polymer ligands, including those that impart amphiphilic properties and that contain reactive functionality, are proposed. These will provide additional insight into the design of pathways to manipulate the assemblies, optimize the functionality of the assemblies, and tailor the ligands to control the assembly process. The proposed studies can impact the design of fuel cell membranes and active layers in photovoltaic devices, addressing one of the five Grand Challenges set forth by the Department of Energy. By controlling the interfacial properties of the nanoparticle assemblies, interfacial and bulk structures can be produced that are far-removed from equilibrium, which addresses yet another of these Grand Challenges. The integration of the synthetic and physics expertise of the PIs is key to the successful execution of the proposed studies.

Structure and Dynamics at Interfaces

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The availability of high-brilliance hard x-ray synchrotron radiation and the advent of novel photon counting area detectors have brought surface x-ray diffraction (SXRD) into a new era. It is now possible to record large numbers of structure factors with much improved reliability within reasonable beamtime durations. As a result, structural determination of the surfaces and interfaces of complex crystallographic systems and heterostructures has now become feasible, especially in conjunction with phase-retrieval methods. One example of the detailed structural information that can be obtained relates to our recent work on heteroepitaxial films of $BiFeO_3$ (BFO). This is one of very few materials exhibiting multiferroic properties at room temperature, being both ferroelectric (Tc ~ 1103 K) and G-type antiferromagnetic (TN ~ 643 K). In its bulk form, BFO possesses a rhombohedrally distorted pseudo-cubic perovskite structure with ferrodistortive displacements along the (111) direction, giving rise to a spontaneous polarization in the same direction. Epitaxial BFO thin films grown under compressive strain ranging from -1.4% on $SrTiO_3$ (STO) to almost -7.0% on $YAlO_3$ (YAO) have been shown to enhance the spontaneous polarization, and the polarization direction is tilted towards the (001) out-of-plane direction, while maintaining a significant in-plane component along the (110) direction.

When grown on substrates exhibiting a four-fold rotation symmetry, BFO films form a total of four distinct ferroelastic domains, each with two possible opposing polarization directions. Previous studies [e.g., Folkman et al.] have reported on the formation of BFO ferroelastic stripe domains (where only two of the four possible domains are present) when growing thick films (200-800 nm) on a substrate with two-fold rotation symmetry and a rectangular surface unit cell, namely on(110) $TbScO_3$ (TSO). In x-ray diffuse scattering measurements, the presence of these ordered domains manifests itself in the appearance of satellite peaks along only one of the in-plane directions and close to the film Bragg peaks. In preliminary measurements of 4 and 10 unit cell (UC) thick BFO films, we observe a strong thickness-dependence of the satellite positions, which proves that this bulk-like structural model does not apply to very thin films. Rather, we believe that the satellite positions are simply a measure of the lateral domain sizes, which increase with increasing film thickness. The structural features characterizing these domains are elusive and require the use of direct phase retrieval approaches to structure determination. We have collected several complete Bragg-rod data sets on the 4 UC samples of BFO on (110) TSO substrates and are in the process of analyzing this data with the COBRA x-ray phase retrieval technique. This method has proved to be successful for other complex oxide heterostructures and we are hopeful that the current system will also be amenable to this powerful analysis approach that we developed for surface/interface structure determination.

Our preliminary analysis indicates that the structural symmetry is tetragonal rather than rhombohedral and that the domain structure is much better ordered than in the bulk. We believe that this highly ordered tetragonal domain structure is the result of epitaxial coherence with the TSO substrate which is preserved when the films are very thin (<10 UC thickness) but relaxes to a less ordered state in thicker films due to the formation of misfit dislocations. Our current work at Sector 33 of the Advanced Photon Source is focused on fully documenting this new structure and checking whether it is also stabilized in ultra-thin BFO films grown on other (110)-oriented perovskite substrates (e.g., $NdGaO_3$, $LaGaO_3$, $DyScO_3$, $GdScO_3$, $SmScO_3$3, and $NdScO_3$). For this purpose, we are collaborating with the MBE group of Darrell Schlom (Cornell) to provide us with high-quality samples of BFO grown on some of these substrates.

Ultrafast Magnetism Dynamics Measured Using Tabletop Ultrafast EUV

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Funding:	$140,000

We are preparing magnetic samples for the investigation of ultrafast nanoscale dynamics by use of extreme ultra-violet (XUV) photons. The high harmonic generation (HHG) photon source for these studies is under development by our collaborators, Professors Murnane and Kapteyn at the University of Colorado, JILA, who are also supported by an additional DOE SISGR program. The samples being prepared include NiFeCu alloy samples for the study of ultrafast demagnetization processes near the Curie temperature, and lithographically patterned nanomagnet structures for the development of "lensless" diffraction imaging methods. Materials are prepared in a variety of deposition tools, include a 7-gun sputtering chamber, and an e-beam evaporation tool. In addition to preparing the samples for XUV study, we fully characterize the samples to completely determine the relevant materials properties that have a bearing on ultrafast demagnetization effects. Characterization includes X-ray diffraction to determine crystalline structure, and SQUID magnetometry to determine magnetic moment, Curie temperature, and critical exponent. In addition, we have developed a process for the fabrication of a silicon nitride phase grating on arbitrary sample materials. The phase grating allows our collaborators at JILA to use the sample as an energy dispersive element in the XUV beam path, which permits the study the ultrafast spin dynamics with elemental specificity. Using this technique, we have found that Ni and Fe that coexist in the same fcc solid solution alloy can each demagnetize in a distinctly different qualitative manner when subjected to an intense 20 fs optical pump pulse. We expect the results from these studies to have practical applications in the development of next-generation hard disk drive technology that utilize the localized application of intense laser light to assist in the data recording process.

Fundamental Studies of the Structural Response of Disordered Materials to High P and T

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Funding: $164,000

Characterizing structural changes accompanying the transitions of liquids, melts and fluids, close to their crystallization or glass transition points and under extreme conditions, is fundamental to understanding and predicting behavior under those conditions. Fragile glass forming liquids, those that show non-Arrhenian behavior close to the glass transition, are especially difficult to study and melt levitation techniques, along with isotope substitution experiments at the Spallation Neutron Source, Oak Ridge Tennessee, allow us to study these liquids deep into the undercooled regime. We have performed neutron diffraction isotopic substitution experiments on aerodynamically levitated droplets of $CaSiO_3$, to directly extract intermediate and local structural information on the Ca environment. The results show a substantial broadening of the first Ca-O peak in the pair distribution function of the melt compared to the glass, which comprises primarily of 6- and 7-fold coordinated Ca-polyhedra. The broadening can be explained by a re-distribution of Ca-O bond lengths, especially towards longer distances in the liquid. The first order neutron difference function provides a rigorous test of recent molecular dynamics simulations and supports the model of the presence of short chains or channels of edge shared Ca-octahedra in the liquid state. It is suggested that the polymerization of Ca-polyhedra is responsible for the fragile viscosity behavior of the melt and the glass forming ability in $CaSiO_3$. X-ray diffraction measurements of these same liquids, again performed on aerodynamically levitated $CaSiO_3$ droplets, have been interpreted using a structurally heterogeneous liquid state model. Molecular dynamics simulations and a comparison to published glass data indicate that changes in the pair distribution function upon cooling the melt are associated with the polymerization of CaO_6. As the high temperature liquid is cooled, diffraction isosbestic points are observed and are assigned to a linear increase in amount of edge shared Ca octahedra. However as the glass transition temperature is approached the magnitude of the structural changes are observed to increase rapidly.

We are now applying some of the lessons learned in these studies to the fascinating subject of “water ropes” formed between two beakers of water when a voltage in excess of 20 kV is applied. Under this extreme condition we and others speculate the water is ordered. Determination of changes in molecular structures is key to understanding water’s properties under these conditions. In order to obtain the best possible data from the area detectors typically used for these studies, which offer high statistical quality from small sample volume and short measurement times, has required intense study of the systematic errors. We just completed a study (Nucl Inst Meth A, (2011), doi:10.1016/j.nima.2011.09.031) outlining correction procedures for obtaining accurate X-ray structure factors from large area detectors, including sub-panel effects, overexcited pixels and careful intensity corrections. Data from glassy $GeSe_2$ and liquid water measured with a Perkin Elmer amorphous-silicon detector are used to demonstrate the effectiveness of these correction procedures. This requires reduction of systematic errors in the measured intensity to around the 0.1% level.

Synchrotron X-ray Based Electronic Structure Study of Correlated Quantum Materials

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Funding:	$410,000

Discovering new phases of matter with useful electronic or magnetic properties is an important goal in modern physics. In the past few years, theoretical developments have uncovered a new phase of quantum matter dubbed "Topological Insulators" (for a review see, M.Z.Hasan and C.L.Kane, Rev. of Mod. Phys. 82, 3045 (2010)). Following our experimental discovery surface states of topological insulators in 2007(actual observation of topological surface states dates a few years back in connection to our work in thermoelectrics carried out under this DOE grant), we have theoretically predicted (using first-principle calculations) as well as experimentally discovered/demonstrated by directly measuring the topological-order character of the edge-spectrum of single-Dirac-cone topological insulators.

Over the last one year under this DOE grant, we have improved a way to probe the spin degrees of freedom in spin Hall like topological phenomena and demonstrated that topological quantum numbers are completely determined from spin-texture imaging measurements. These spin-sensitive results constitute the observation of surface electrons collectively carrying a topological-Berry's phase and definite spin chirality in many topological materials. These are the key electronic properties for realizing topological quantum information bits using a topological surface. We have also demonstrated that the topological-order can be maintained at room-temperature without magnetic field, the absence of backscattering or the protected nature of the states and that the materials can be driven to the topological transport regime paving the way for realizing some high-energy-physics-like experiments at table-top settings with wide tunability and systematic quantum control. We have further discovered and systematically studied several new classes of topological insulators in ternary spin-orbit systems such as the Half-Heuslers, Li-Intermetallics, TlBiSe2-class and in many other compounds. We have also discovered Topological-Order in a doped topological insulator as it becomes a superconductor.

Fundamental Mechanisms of Roughening and Smoothing During Thin Film Deposition

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Funding:	$183,000

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. This project 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. In the case of sputter deposition, the objective of the work is to develop an improved theory of smoothing of amorphous film surfaces during sputter deposition that includes the effects of smoothing and roughening processes in a realistic way, and to extend these studies to deposition of epitaxial films. In the case of laser deposition, an understanding of the atomic-scale surface smoothing processes that operate during the deposition of single crystal layers is sought. Thin film growth is performed in a vacuum deposition system with the capability to perform time-resolved x-ray diffraction experiments during the deposition process. These measurements are used to reveal fundamental aspects of surface smoothing processes. Control and manipulation of smoothing processes on surfaces during thin film deposition is a key challenge in technology, and touches on a wide variety of applications that employ ultra-thin layers, 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.

This funding is being used to support one postdoctoral associate and one graduate student for three years. The film growth efforts on Pulsed Laser Deposition and Sputter Deposition will be continued, and the theme of nanostructured surfaces and films will be extended to growth and characterization of epitaxial layers. We are particularly interested in creating novel nanostructures by exploiting effects that occur during off-normal deposition, or by deposition of nanometer-scale clusters. The work complements several large-scale facilities under development at BNL, including the NSLS-II, the Center for Functional Nanomaterials, and existing Molecular Beam Epitaxy and Pulsed Laser Deposition growth efforts.

Dynamics and Extreme Conditions in Complex Oxide Heterostructures

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Funding:	$196,000

We are developing and applying synchrotron x-ray scattering probes that will enable us to understand the behavior of complex oxide thin film heterostructures in new regimes of short times and high electric fields. The time resolution of synchrotron techniques is an excellent match for fundamental scientific problems emerging in heterostructures comprised of complex-oxide dielectrics and ferroelectrics. Simultaneous advances in x-ray scattering techniques and in the growth of nearly crystallographically perfect epitaxial structures now permit us to achieve the high fields necessary to probe large piezoelectric expansions and compressions, to examine electrostriction in high fields, and the time resolution required to understand the dynamics of domains and structural transitions in superlattices. These problems have been the subject of tremendous recent theoretical advances, including the potential to predict nonequilibrium structures extremely accurately, but present serious challenges to existing experimental probes. Addressing these challenges is possible with new time-resolved x-ray scattering techniques, which will be critical to future scientific advances in describing and exploiting the materials under nonequilibrium conditions.

From the perspective of x-ray scattering, the required developments include advances in time resolved x-ray nanodiffraction and diffuse scattering techniques, the interpretation of diffraction and diffuse scattering data, and the preparation of optimized complex oxide capacitor samples. We will improve the time resolution of nanodiffraction and domain diffuse scattering techniques by developing high-bandwidth electronic device structures, refining the synchronization between x-ray and electrical pulses, and by developing strategies for the future use of emerging sources with inherent pulse durations better than the 100 ps-pulses available at synchrotron light sources. Our development of these x-ray scattering probes presents the unique opportunity to conduct several experiments probing the physics of electrically driven complex oxides.

The new capability to perform scattering studies on materials in high electric fields greatly extends the range of non-equilibrium conditions accessible to structural techniques. We have already demonstrated that we can induce transient piezoelectric expansions of 2% or more, and we now will test theoretical findings that such large piezoelectric strains can result in enhancement or saturation of electromechanical distortion or induce structural phase transitions. Short electric field pulses do not provide sufficient time for ferroelectric polarization to proceed switching via domain wall motion, and as a result, the structure of ferroelectrics can be probed in a unique un-switched polarization state if electric-field pulses have sufficiently brief duration. We will use this effect as the means to search for the intrinsic coercive field for polarization switching in oxide ferroelectrics, which has previously been obscured by slow phenomena such as domain wall motion. We further will extend these capabilities to conduct a study of electrostrictive distortion in high electric fields.

The dynamics associated with domains and field-induced changes in crystalographic symmetry in complex oxide superlattices occur at timescales ranging from hundreds of picoseconds to many nanoseconds, an excellent match for time resolved x-ray scattering. Diffraction from superlattices provides unique additional structural information that can be used to resolve structural changes at the length scale of individual layers within the superlattice. Although control of the material properties in dielectric/ferroelectric superlattices using strain and electric fields has been well documented, recent predictions of lowered crystallographic symmetry and unusual dynamical phenomena in these materials are as yet untested.

Probing Surfaces and Nanostructures with Surface X-ray Diffraction: Application of a Direct Method for the Visualization of Surfaces

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Funding:	$189,000

The principal aim of the project is to investigate surface structural arrangements using a combination of surface x-ray diffraction (SXRD) and novel tools and algorithms for interpreting SXRD data. Other analytical techniques are also invoked to help supplement the scattering data. The materials systems of present focus include the surfaces of polar oxides and their interfaces with liquid water. Polar oxide surfaces, in which the surface plane is parallel to planes of anions and cations, have an inherently high surface energy and frequently exhibit interesting phenomena such as reconstruction, surface electric fields, and electronic rearrangements. These reconstructions are often stable for extended periods in air and/or under water layers. Note that growth of most oxides via certain techniques, such as atomic layer deposition (ALD), is inherently along the polar direction. Beyond being of interest in their own right, polar oxide surfaces, by their nature, interact strongly with a polar liquid medium, such as water.

In the period described, we have conducted SXRD investigations at Argonne National Laboratory of reconstructed MgO(111)-(rt(3)xrt(3))R30 and ZnO(000-1)-(rt(3)xrt(3))R30 surfaces prepared by furnace annealing, and have begun to apply direct-method algorithms to determine their atomic structure. We have also investigated the structure of the interface between a bulk water layer and a MgO(111)-(rt(3)xrt(3))R30 surface. In addition, we have conducted atomic force microscopy (AFM) and low energy electron diffraction (LEED) studies at the University of Wisconsin-Milwaukee of the affects of annealing time, temperature, and atmosphere on the morphology and structure of the annealed surfaces. Also, the composition of outermost layers of the reconstruction is of interest, in particular the presence or absence of hydrogen, is a critical question that is difficult to address by standard analytical methods or by SXRD. Therefore, we have conducted nuclear reaction analysis (NRA) and elastic recoil detection analysis (ERDA) at Pacific Northwest National Laboratory to address the question of H coverage.

Both LEED and SXRD data need to be related to the surface structures. This requires data interpretation by theory. In the case of the strongly multiple-scattering LEED, the data interpretation needs a trial-and-error approach of repeated guessing of the structure and comparisons of data simulations with actual data, with a monitoring performed by means of a reliability factor (or R-factor). However, SXRD can be largely modeled by a more tractable single scattering theory. This allows the development of an algorithm for finding the surface electron density directly from the measured data, using a knowledge of the bulk structure and an approximate knowledge of the extent of the surface region. We are currently working on generalizing the computer program to cover all possible symmetries and surfaces. The case of our present interest, the (rt(3)xrt(3)) (111) surface, is particularly challenging as the surface unit vectors are non orthogonal and because the unit vectors of reciprocal space are not coincident with those of real space. We are working on developing a user friendly version of this code for general use.

From our SXRD investigations of the dry MgO(111)-(rt(3)xrt(3))R30 surface, we have been able to determine that the structure differs in important ways from any of the structures proposed in the literature. While we have not yet been able to determine the structure uniquely, our results appear to be consistent with an atomic bilayer of atoms in the wurtzite phase (instead of the native rocksalt structure). Another principal finding is that, in the presence of bulk water, a few layers of water at the interface of this surface attains a lateral periodicity the same as the reconstructed surface. That is, the reconstructed surface acts as a template to imbue lateral ordering on the water. This ordering had been previously observed in the vertical direction, but only rather indirect evidence had been found for any lateral ordering. Finally, we have found, using ion-beam analysis techniques, that very little H is present at the surface of a reconstructed MgO(111) surface; we detected only approximately 5% of a monolayer of H on a freshly prepared surface, and about a 23% of a monolayer on a surface that had been exposed to air for 18 months. It does not appear that H plays a significant role in the reconstruction.

Dynamics of Block Copolymer Nanocomposites

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Funding:	$189,000

The goal of this project is to establish and investigate the basic physical principles underlying the equilibrium structures and dynamics within block copolymer-nanoparticle nanocomposites. This new understanding will facilitate the design and creation of robust and stable nanocomposites with desirable properties. Recent progress includes the following:

(1) Creation and characterization of polymer-coupled CdS nanoparticles: We have successfully implemented protocols at Yale to create CdS nanoparticle-block copolymer micelles. In which CdS nanoparticles are co-located with a P2VP micellar cores with a polystyrene micellar shell. Electron microscopy measurements confirm the existence of such micelles.

(2) XPCS study of the equilibrium dynamics of the disordered phase of a polystyrene-polyisoprene block copolymer melt: We carried out for the first time a successful XPCS study of the temperature-dependent dynamics of the disordered phase of a polystyrene-polyisoprene block copolymer melt (PS-b-PI). We carried out SAXS and XPCS measurements to characterize the static and dynamic structure factors within the disordered phase. In fact, it was only possible to measure an XPCS signal near the peak of the static structure factor, because of the weak signal. Nevertheless, this measurement represents the first instance for which the molecular scale dynamics in a block copolymer melt, that is not in a microphase-separated regime, has been determined. Currently, a report of the data is being prepared for publication.

(3) Measurements of the orthorhombic FDDD phase in a PS-b-PI block copolymer melt: Serendipitously, we found that our PS-b-PI samples exhibit the orthorhombic Fddd phase, first discovered in triblock copolymers by Frank Bates' group, and more recently predicted and then seen in PS-b-PI melts. This may prove a useful and interesting template for future decoration by nanoparticles.

(4) Realization of CdS nanoparticle-decorated PS-b-PI nanocomposites and SAXS and XPCS studies of the equilibrium dynamics of the disordered phase of a polystyrene-polyisoprene block copolymer melt decorated by CdS nanoparticles: We have successfully incorporated our CdS nanoparticles into a PS-b-PI block copolymer melt. We have carried out SAXS and XPCS from such a material in the disordered phase of the block copolymer. The SAXS experiments reveal a clear signature of the CdS nanoparticle-carrying micelles, while a comparison of the XPCS intensity autocorrelation functions obtained at the block peak of the block copolymer's static structure factor in the disordered phase reveals that the shape of the correlation function is different in the two cases, indicating that the presence of nanoparticles affects the block copolymer's equilibrium dynamics. Additional measurements indicate that the nanoparticles are dynamic within the block copolymer matrix. In turn, this confirms that the nanoparticles are not aggregated, but indeed are "floating" freely. These nanoparticles we expect to preferentially wet PS. Therefore, in ordered phases of PS-b-PI, we expect these nanoparticles to preferentially go into the galleries composed of PS-rich regions. Thus, in a lamellar phase, we expect to confine the nanoparticles to the two-dimensional PS-rich galleries. Similarly, in a hexagonal phase with a PS-minority phase, we

expect to confine the nanoparticles to the one-dimensional PS-rich cylinders. The next step, therefore, is to investigate what happens to the SAXS and XPCS in the ordered phases of PS-B-PI.

DOE National Laboratories

Synchrotron Radiation Studies

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Funding: $2,050,000

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 understanding dynamics in the reactive environments of crystal growth and catalysis. Finally, we are performing the first atomic resolution x-ray photon correlation spectroscopy measurements on simple liquids to observe their diffusive and vibrational modes near the glass transition temperature. Throughout this research, we strive to develop a fundamental understanding of materials physics while also laying a solid foundation for in-situ materials science at the DOE Scientific User Facilities. The in-situ techniques enabled by the latest x-ray sources are important components in the transition of materials development from an empirical technology to a control science—a crucial transition if we are to meet the need for new, exceptional materials for energy applications.

Towards Understanding and Control of Nano-Scale Fluctuations in Strongly Correlated Electron Systems

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Funding:	$100,000

Nanoscale fluctuations of structure, charge and spin are important in determining the properties of many strongly correlated electron systems but are hard to study experimentally. This program seeks to bring together expertise in a number of different experimental areas to give new insights into strongly correlated electron physics through studies of the fluctuations. There are two main activities that are part of this proposal. The first is to develop atomic pair distribution function and related methods and apply them to study fluctuations in strongly correlated electron systems. The second is to use a range of complementary expertise and techniques to understand the role of fluctuations. Initial projects include studies of electronic phase separation in the manganites combining dark field electron imaging, resonant x-ray imaging and PDF, characterization of stripe fluctuations in the nickelates, and the search for broken symmetry states in the pseudogap region of the cuprates. This Includes nematic and smectic states, competing interactions leading to nanoscale phase separation in a model system, Cr doped copper iridates, and finally, studies of nanoscale fluctuating dipoles in thermoelectric PbTe.

A long term goal is to be able to use PDF techniques to study thin films of SCES materials grown by MBE. Such studies will be carried out using both electron diffraction and high energy x-ray scattering.

X-Ray Scattering

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Funding:	$1,195,000

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 synchrotron-based x-ray scattering techniques. In FY 2011, a number of important results were obtained. These included the first results from a new soft x-ray resonant scattering chamber built by the group. In particular, studies on two doped cuprates; $La1.875Ba0.125CuO_4$ (LBCO) and $La1.48Nd0.4Sr0.12CuO_4$ (LNSCO), compared the modulation of the doped holes (stripes) in the two cases and found them significantly stronger and better correlated in the LBCO system than in the LNSCO system. Furthermore, it was found that the amplitude of the modulation remained constant as a function of temperature in LBCO up to the low-temperature tetragonal (LTT) structural transition. These results are important both for the light they shed on the stripe phase, which competes with high-temperature superconductivity, and for future searches for stripe-like correlations in the pseudo-gap phase - scheduled for FY 2012. In related time-resolved experiments performed at the LCLS, we showed that under excitation with mid-IR photons tuned to an in-plane Cu-O bond stretching phonon, that the electronic modulation melted on ultrafast time scales (sub-500 fs), while the LTT phase melted on much slower time scales (> 10 ps). These results show that the stripe modulation is not a direct consequence of the LTT phase and may make possible connection to observations of light-induced superconductivity in related materials. In other work performed in the new chamber at NSLS, studies on manganite multiferroics revealed a purely electronic mechanism for ferroelectricity in YMn_2O_5 arising from spin-dependent hybridization between the Mn and O, as revealed by resonant scattering at the oxygen K-edge.

Finally, a new program was begun on the physics of iridium-based transition metal-oxide compounds. These 5d systems are interesting because the larger spin-orbit coupling, relative to their 3d transition metal cousins, can drive weakly correlated systems to the strongly correlated limit. This coupled with large exchange interactions, quantum isospins and low dimensionality makes them a rich source of new physics. We have carried out elastic scattering measurements on Na_2IrO_3, a candidate quantum spin liquid material. In contrast to expectations, long range magnetic order was observed and, in combination with ab initio theory performed by BNL theory group, the magnetic structure was determined. Inelastic scattering studies of this, and the related material Sr_3CuIrO_6, reveal the d-d excitation spectrum, which allows the spin-orbit coupling and the crystal field splitting to be determined. In addition, we have observed the low energy magnetic excitations of the j1/2 isospin in Sr_3CuIrO_6. These are highly dispersive along the chain direction, with a bandwidth of 20 meV and a gap of 30 meV. These results allow a complete modeling of the spin and orbital degrees of freedom in this model compound and we conclude that an atomic, spin-orbit coupled description works well.

Fundamental Structural Studies of Hybrid Biomolecular Materials Using Scattering Techniques

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Funding:	$500,000

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 on 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 what is seen in nature.

Ultrafast Materials Science

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Funding:	$1,007,000

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 on 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 onto the emergent physics of complex materials and nanostructures.

Ultrafast Optical Spectroscopy: Investigating Dynamic Correlations in Complex Materials

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Funding:	$300,000

The power of ultrafast optical spectroscopy (UOS) lies in its ability to temporally resolve phenomena at the fundamental timescales of atomic and electronic motion, and to unravel the competing degrees of freedom that ultimately determine mechanism and functionality in complex materials (CM) ranging from transition metal oxides and f-electron intermetallics, to organic materials such as polymers, polyacenes, or even DNA. The sub-picosecond temporal resolution, combined with spectral selectivity available with UOS, enable studies of electronic, spin and lattice dynamics, and more importantly, of the dynamics of the coupling between these degrees of freedom. UOS thus complements both 'static' techniques such as time-integrated optical spectroscopy, and dynamic techniques such as inelastic neutron scattering, presenting an excellent experimental alternative for studying temperature-dependent changes of the low-lying electronic structure of complex materials. Building on our forefront theoretical and experimental expertise and capabilities in ultrafast materials science, we propose a closely coupled theoretical/experimental program that uses and develops UOS to investigate and understand the character of competing spin, charge, lattice, and superconducting interactions in complex materials. Our goal is to continue to explore and advance the utility of such techniques with the primary objective of providing unique insights into the fundamental functional properties of complex materials. 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 such gaps; multiferroics to investigate the role of competition and coexistence of the orders; oxides and manganites to study polaron formation and their coupling to other quasiparticles; and graphene to reveal ultrafast non-equilibrium dynamics of photocarriers in graphene's unique relativistic band structure.

X-Ray Scattering and Microscopy

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Funding:	$1,475,000

The goal of this project is to gain understanding of 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 both the development and the application of neutron microfocusing optics at the Spallation Neutron Source (SNS). High-pressure magnetic scattering studies of magneto-volume effects associated with 3d invar type alloys including Fe-Cr, Fe-Mn, and Fe-Ni 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 enable 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.

Electronic and Magnetic Structure of Quantum Materials

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Funding: $2,278,000

The Electronic and Magnetic Structure of Quantum Materials project focuses on the physics of correlated materials, with a strong emphasis on coupled theoretical and experimental activities, to probe and understand electronic and magnetic structure of complex materials. We study the fundamental principles governing the emergence of novel phases of quantum matter in correlated materials that derive from the strongly intertwined charge, spin, orbital, and lattice degrees of freedom. Our efforts aim to address the Grand Challange of “emergence” as well as a number of Basic Research Needs areas for energy applications. The complex materials targeted for this research, for example transition metal oxides, will have strong ties to superconductivity and related phenomena, such as Solid State Lighting, for example. The insights, the methodology, the experimental and theoretical tools developed will also contribute to the emergence of a general theme in modern research: transformation from science of observation to science of control.

Both experimental and theoretical advancements of x-ray spectroscopy and scattering techniques offer unprecedented insights into electronic and magnetic structures in materials, and span areas from fundamental science to applied materials and devices. Our intellectual emphasis is to study novel charge, magnetic, orbital and superconducting order in a number of novel materials. The tools and methods we use are based on photon experiments/simulations.

Our project works collaboratively as a unit, resulting in 17 high profile papers in our focused research areas (*Physical Review Letters, Science and Nature* articles) in FY 2011 and more than 11 co-authored papers. We work collectively with all the other SIMES projects (e.g., more than 16 co-authored papers across units, leveraging activities in sample growth and fabrication, photon-science based expertise, and theoretical simulation and modeling) and collaborate closely with the Advanced Light Source (over 18 joint publications).

We take advantage of two important DOE photon science user facilities at SLAC (SSRL and LCLS), related in-house experimental tools, as well as other cutting edge theoretical capabilities both locally at SLAC and NERSC grid computing. We also leverage efforts with other DOE user facilities, such as the Advanced Light Source at Berkeley. The advanced X-ray capability is essential to address all five Grand Challange problems because of its ability to reveal atomic and electronic structures on ultra small and ultrafast length and time scales.

Interfaces and Catalysis for Energy Conversion and Storage

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Students: 5 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding: $879,000

This program addresses chemical transformations involving interfaces where catalysis occurs or the change of materials under high pressure. 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 and "matter in extreme conditions" regarding systems under high pressures. 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.

Magnetization and Dynamics

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Students: 1 Postdoctoral Fellow(s), 5 Graduate(s), 0 Undergraduate(s)
Funding: $1,398,000

This project 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 project is to learn how to manipulate/control ferromagnetism using LCLS, SSRL and Squids (complementary time & length scales) to determine speeds for magnetic switching and to characterize transient spin states far from equilibrium.

The 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 (Durr, Scherz, Stohr), along with the magnetic characterization using scanning-probe-based magnetic imaging, particularly scanning SQUID microscopy (Moler). XMCD and SQUIDs provide complimentary information in that XMCD provides chemically specific (spin & 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. This activity of the investigation of magnetic domains complements the activities of magnetic interaction at atomic level in Spin Physics project through nanoscale imaging, and is important for technology.

Spin Physics

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Funding: $415,000

The Spin Physics program consists of two closely related subtasks. The first subtask of Orenstein and Zhang investigates spin transport in semiconductors and topological insulators. The second subtask of Goldhaber-Gordon and Manoharan directly measures and manipulates low-dimensional spin, isospin, and electron correlations using scanning probes (scanning tunneling microscopy and spectroscopy [STM/STS], a new tool termed "Virtual STM," and Scanning Gate Microscopy) via the precise control of nanoscale geometry through nanofabrication and nanoassembly.

Time-Resolved Soft X-ray Materials Science at the Linac Coherent Light Source and the Advanced Light Source

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Moore, Robert, SLAC NATIONAL ACCELERATOR LABORATORY
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Funding: $1,747,000

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 Challange problems of “emergence” and nonequilibrium dynamics, and to develop model systems for deep insights on materials for energy conversion, transport and efficiency. We are building a time-resolved, optical-pump and x-ray probe, with 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 are performed in parallel to gain further insight into the experimental data and establish formalism for describing non-equilibrium physics of strongly correlated materials. The program consists of a local core team made of researchers from SLAC and Lawrence Berkeley National Laboratory, enhanced by a strong web of collaborations with scientists from other institutions.

II. CHEMICAL SCIENCES, GEOSCIENCES, & BIOSCIENCES DIVISION

AMO Sciences

Institutions Receiving Grants

Coherent and Incoherent Transitions

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Funding:	$80,000

TRANSITIONS THROUGH A CHAOTIC SEA

During the past year, we further extended this area by investigating molecular ro-vibrational energy transfer and transfer of energy through an inflection point in the non-twist map. For our molecular studies, we (1) used HF as a test system to show that we could transfer the molecule from the ground vibrational state to v = 4 with near unit efficiency, (2) performed quantum calculations in full 3-D and showed that the final angular momentum distribution is restricted if the initial state is also restricted in J, (3) performed calculations for a thermal distribution of J, and (4) studied the situation where the energy and frequency do not have a monotonic relation. Systems with a monotonic relation are easy to manipulate with chirped pulses (quantum mechanically this corresponds to systems where the energy level spacing either decreases with increasing energy or the spacing increases with increasing energy). The inflection with energy prevents schemes like vibrational ladder climbing from working. We showed that adiabatically chirping through a multiphoton resonance between two states would allow us to transfer population through the inflection region.

FLUORESCENCE AS A PROBE OF ULTRACOLD PLASMAS

In a series of studies with Bergeson's experimental group, we have used experiments and simulations to investigate the early time properties of ultracold neutral plasmas. The technique uses fluorescence from excitation of the ionic core to measure the ion velocity using simulations as a guide. We focused on the earliest times, when the plasma equilibrium is evolving and before the plasma expands. To correctly model the fluorescence, we solved the optical Bloch equation for each ion in the simulation. In the most recent paper, we investigated the density and temperature scaling of the disorder-induced heating of the ions. We did not find the expected scaling as the electron temperature was decreased to ~0. The lack of scaling is interesting because our studies were at the earliest times where simple physics should be manifest.

EFFECT OF PLASMAS ON PERTURBER STATES IN RYDBERG SERIES

Collaboration with scientists interested in atomic processes in plasmas led to a novel idea about states imbedded in Rydberg series when the atom is in a plasma. Resonance states in atoms or ions at low energies can control the rates of important plasma processes (e.g., dielectronic recombination). We examined the role of states at negative energies just below the ionization threshold of the recombined system and found that they can contribute as much, or more, to recombination as positive energy states because the Rydberg states are constantly being populated and mixed by the constituents of a plasma. We found that these states can substantially change thermally averaged rate coefficients and could remove much of the sensitivity of rates to the exact energy of states.

ELECTRON IMPACT DOUBLE IONIZATION/THREE ELECTRON CONTINUA

We continued our studies of electron impact double ionization of atoms. We studied the double ionization of B+ ion using the non-perturbative close-coupling method between the double-ionization threshold of 63.1 eV and the 1s ionization threshold of 218.4 eV. We computed the indirect single ionization-autoionization cross section using the perturbative distorted-wave method between the 1s ionization threshold of 218.4 eV and 750 eV. We compared our results to a crossed-beam experiment over the entire range and found excellent agreement over the whole range.

Ultrafast Holographic X-ray Imaging and its Application to Picosecond Ultrasonic Wave Dynamics in Bulk Materials

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Students:	0 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding:	$140,000

A new x-ray absorption spectrometer was developed at the Advanced Photon Source, sector 7, ID-C and used for x-ray absorption measurements of the ligand substitution reaction of Fe(CO)5 in ethanol with 2ps temporal resolution. Based on this work we applied for Partner-user status at the APS, which recently was granted for the period from the summer 2011 to the summer 2013. During this time we will receive 10% of the beamline’s beamtime for further development and application of the picosecond x-ray instrument.

Our work on x-ray phase contrast imaging will be continued with the development of a novel x-ray imaging concept we named Spatial Frequency X-ray Heterodyne Imaging (SFXHI). 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 3 orders of magnitude larger than for conventional x-ray absorption imaging. For high emittance x-ray sources or motion blurred samples, the SFXHI 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.

Electron-Driven Processes in Polyatomic Molecules

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Funding:	$135,000

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 an 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. 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.

Few-Body Fragmentation Interferometry

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Funding:	$96,000

We continue our work to extract basic understanding and quantum control of few-body microscopic systems based on our long-time experience with more conventional studies of correlated electrons and ions. Given the enormous advances over the past 20 years to our understanding of quantum correlations with photon interferometry, AMO collision science generally is ready to move beyond the one-particle, single-port momentum detection that has dominated collision physics since Rutherford. A recent, impressive, beautiful example is that of a direct measurement of the real and imaginary parts of a photon's transverse wavefunction reported in *Nature* (2011). These sorts of observations involving `quantum weak measurements' (Aharonov-Vaidman) should in principle be just as doable with massive particles. Nevertheless, our familiar theoretical tools for collision theory will need to be upgraded to incorporate these more generalized measurement formalisms and ultimately to provide incentive for a new generation of experiments.

On a broader scale, fresh insight into few-body science at molecular nano levels will be a critical component of ongoing national and international efforts to establish sustainable energy and environmental 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 in this project is theoretical, our interest in these topics remains strongly 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 emphasis on reaction imaging while pursuing longtime work on collective Coulomb excitations. As in the past, we continue to place strong priority on research relevant to experiment.

Electron-Driven Excitation and Dissociation of Molecules

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Funding:	$95,000

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

Theory and Simulation of Nonlinear X-Ray Spectroscopy of Molecules

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

The stimulated x-ray Raman spectroscopy (SXRS) signal of *trans*-N-methylacetamide (NMA), a small organic molecule used as a convenient model system for the peptide bond forming the backbones of proteins, was calculated using a description of core excitations at the static-exchange (STEX) level, which offers a much improved representation of orbital relaxation effects and of the virtual orbitals to which the core electrons are excited than the equivalent-core approximation (ECA) used earlier. The signal obtained in response to two soft x-ray pulses reveals the dynamics of valence-electron wave packets prepared and detected in the vicinity of a selected atom (either nitrogen or oxygen).

Closed-time-path loop diagrams were developed for interpreting this signal. Orbital relaxation effects following core electronic excitations were studied by comparing the N and O K-edge x-ray absorption near-edge structure (XANES) at the ECA and STEX levels. The attosecond snapshots of electron dynamics provided by resonant x-ray techniques call for developing real time/real space visualization schemes. The evolving electronic charge densities, consisting of several entangled valence particle–hole pairs, as well as the electronic coherence of the doorway and the window created by the two pulses were visualized using a time-dependent basis set of natural orbitals. This picture goes beyond the time-resolved charge density provided by electron diffraction and carries valuable many-body information about electron correlations as well.

Another effort focuses on the development of multidimensional attosecond photoelectron spectroscopy with shaped pulses and quantum optical fields. Photoelectron spectroscopy is a powerful tool for probing orbital energies in molecules and crystals. In time resolved photoelectron spectroscopy (TRPES), the system is prepared in a nonequilibrium state by a laser pulse, evolves for a delay time *t,* and is eventually probed by detecting the electrons generated by a second, ionizing, and pulse. The distribution of the electron kinetic energy reveals underlying electronic and vibrational dynamics through a parametric dependence on the time delay. Multidimensional TRPES signals induced by a series of temporally-well separated pump pulses with variable delays followed by a final ionizing detection pulse were predicted and analyzed.

Electron/Photon Interactions with Atoms/Ions

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Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $80,000

Very recently the same fundamental mechanism that underlies the well-investigated muon-catalyzed nuclear fusion using deuterium (d) and tritium (t) has been proposed to drive nanoscale catalysis. Namely, the fundamental atomic mechanism responsible for the oxidation of water to peroxide has been attributed to the interplay between Regge resonances and Ramsauer-Townsend (R-T) minima in the electron elastic total cross sections (TCSs) for Au and Pd atoms, along with their large electron affinities. Furthermore, transition state calculations on Au^- and Pd^- anion catalysis of H_2O have been performed using dispersion-corrected density-functional theory. These anions speed up the reactions by lowering the activation energy, with the Pd^- anion accomplishing the catalysis by a factor of about three times faster than that by the Au^- anion. The mechanism involves anionic molecular complex formation, with the Au^- and Pd^- anions breaking up the hydrogen bond strength in the two water molecules, permitting the formation of the peroxide in the presence of O_2. The formation of these anion complexes in the transition state, with the interaction of the Au^- and Pd^- with H_2O being comparable to the strong hydrogen bond, has been identified as the mechanism for breaking up the H-O bond strength in the catalysis of H_2O_2 using the Au^- and the Pd^- anions. Thus, the crucial link between low-energy electron elastic scattering resonances (maxima and minima in the electron elastic scattering TCSs) and low-energy chemical reaction dynamics has now been fully established, a truly theoretical breakthrough. The discovery allowed us to use the Au TCS as a benchmark for nanocatalysts, leading to the identification of Pt, Ag, Ru, Tl, At, etc. as possible candidates for nanocatalysts for various substances. Also, we can now understand the experiments with ozone gas that demonstrated that bacteria and viruses were being torn apart, the Ag acting purely as an extremely efficient oxidative catalyst. The Ag^- anion acts similarly to the Au^- and Pd^- anions; it oxidizes the H_2O to H_2O_2, a disinfectant, the desired oxidation product for bacteria or viruses destruction. Contrary to general beliefs, the atoms Cd, Mn, Ni and Zn are predicted to form stable negative ions in slow electron collisions; and they could thus be useful as nanocatalysts. Knowledge of the cross sections for these atoms is also important in understanding heavy fermion metals. We have also investigated the photoionization of endohedral fullerenes using our recently developed random phase approximation with exchange method, and our model potential for the fullerene.

Generation of Bright Soft X-Ray Laser Beams

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Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$145,000

This project addresses the challenge of the efficient generation of bright x-ray laser beams. The great interest in high intensity soft x-ray and x-ray laser light that has motivated the commissioning of free electron lasers also motivates the development of more compact and more widely accessible table-top soft x-ray lasers for applications.

Amplification in inverted atomic transitions can lead to the generation of bright x-ray laser pulses that are uniquely characterized by the large number of photons in a narrow bandwidth. Table-top soft x-ray experiments are conducted at Colorado State University to advance the development of intense plasma-based table-top lasers to shorter wavelengths. The work combines experiments with detailed hydrodynamic/atomic physics simulations to extend gain-saturated table-top lasers to wavelengths shorter than 10 nm. The scheme is based in the generation of transient population inversions by collisional electron impact excitation of multiply ionized ions in hot-dense plasmas created by a compact optical laser. The effort initially focuses in demonstrating an 8.8 nm wavelength laser in the 4d 1S0-4p 1P1 transition of nickel-like lanthanum (29 times ionized lanthanum atoms), to subsequently extend the results to the demonstration of table-top lasers at increasingly shorter wavelengths by isoelectronic scaling to higher Z ions. Experiments have succeeded in obtaining gain-saturated operation of an 8.8 nm wavelength table-top laser at 1 Hz repetition rate. Laser pulses of 2 μJ energy were generated at this wavelength. Isoelectronic scaling of this result also led to the observation of laser amplification at wavelengths down to 7.9 nm for the first time on a table-top. The high plasma density at which these new 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. The implementation of atomic lasers pumped by the bright x-ray pulses produced by the LCLS is also addressed. This free electron laser is designed to operate in a self-amplified spontaneous emission mode. This produces x-ray pulses that fluctuate in wavelength from shot to shot and which have a very limited temporal coherence. Atomic laser schemes pumped by these pulses can generate x-ray laser pulses with fixed wavelengths, significantly narrow linewidth, and improved temporal coherence.

Experiments are also conducted to characterize the output of the table-top soft x-ray lasers for applications. These include the measurements of the far field pattern and the coherence properties.

Properties of Actinide Ions from Measurements of Rydberg Ion Fine Structure

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Funding:	$130,000

This program measures certain properties of multiply-charged thorium and uranium ions by attaching a single electron to the ion of interest in a high angular momentum Rydberg state and measuring the details of that electron's binding energy. Those details reflect the long-range interactions between the Rydberg electron and the core ion whose strength is controlled by core ion properties such as polarizabilities and permanent moments. The particular ions targeted for study, Rn-like U^{6+} and Th^{4+}, Fr-like U^{5+} and Th^{3+}, and Ra-like U^{4+} are selected because they are common charge states of U and Th in chemical compounds. Because they are highly relativistic multi-electron ions, calculations of their properties are suspect until tested by measurements. This program will provide some of the first experimental measurements of the properties of these ions. These will serve the dual purpose of providing data that can be directly useful to actinide chemists and benchmark tests of relativistic atomic structure calculations.

Coherent Control of Electron Dynamics

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Funding:	$150,000

Advances in laser technology and computing power enable us nowadays to observe and control electron dynamics and the exchange of energy between electrons as well as between electrons and nuclei in real time. In this project, we theoretically analyze on the basis of computer simulation features, prospects and new strategies to achieve this goal of attosecond physics (1 as = 10^{-18} s). Our activities can be summarized in the following sub-projects.

We analyze coherent control schemes for the transition between different electronic states in an atom or molecule in the temporal domain. To this end, we solve the time-dependent Schrodinger equation for atomic and molecular model systems interacting with laser fields at different wavelengths. Our results show how in a pulse train the (constructive or destructive) interference between the transition amplitudes induced by the individual sub-pulses lead to maxima and minima in the final excitation probabilities. Different scenarios for atomic bound-bound and bound-continuum as well as molecular bound-bound and bound-dissociative state transitions are considered and analyzed.

Next, we analyze the laser-driven electron dynamics in nature's simplest molecule, the hydrogen molecular ion, on an attosecond time scale. Our simulations show the counter-intuitive result, that the electron can leave the molecule not at the maxima of the oscillating field, as assumed over many years, but at several other time instants during the laser pulse. In collaboration with an experimental group from Frankfurt/Germany we were able to confirm this unexpected dynamic as it is mapped onto the momentum distributions of the electron in the continuum. We are now in the process of investigating whether or not similar dynamics can be found in more complex molecules as well.

Finally, we study the coherent control of the internal quantum state of a molecule (vibration/rotation) based on recently developed laser systems in the infrared. It is found that the population transfer between two vibrational states can be strongly enhanced if the energy difference between the states equals twice the photon energy of the laser. We are in the progress of extending these control schemes towards the dissociation and ionization of the molecule.

Molecular Dynamics Probed by Coherent Electron and X-rays

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding:	$170,000

The goal of this work is to develop novel short wavelength probes of the fastest coupled electron and nuclear dynamics in atoms and molecules. We made several exciting advances that uncovered complex molecular dynamics using ultrafast, coherent, x-rays and electrons emitted during the high harmonic generation (HHG) process. First, we captured chemical dynamics initiated by ionizing radiation, inaugurating the field of radiation femtochemistry. This work immediately uncovered new and unanticipated pathways for the breakup of highly excited molecules, and was published in *Science*. Second, we showed that HHG from large-amplitude vibrations in a dimer molecule can reveal information about the cation states in molecules. The use of a dimer undergoing large structural changes pushes the state-of-the-art in theory and experiment for understanding molecules in strong fields. Third, we found that HHG from molecules can be strongly elliptically polarized even when driven by linearly polarized laser fields. This finding, published in *Physical Review Letters*, corrected previous work by other groups by taking higher signal-to-noise data and carefully analyzing the polarization state. These results have implications for understanding molecules in strong fields because they cannot be explained by simple strong field and single active electron models. Finally, we showed for the first time using any probe that many higher-order rotational revivals can be observed (up to order 12) in HHG from aligned molecules. These data make it possible to extract the underlying electronic dipole elements for HHG, revealing that the electron in the continuum can absorb angular momentum from the photon field.

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

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Funding: $120,000

One of the powerful features of two-dimensional Fourier transform (2DFT) spectroscopy is its ability to separate homogeneous and inhomogeneous broadening and measure both linewidths. This capability is not surprising as 2DFT spectroscopy is closely related to photon echo spectroscopy. In prior work, we had used an approach developed by our theory collaborators, namely measuring the frequency difference between positive and negative peaks in a phase resolved spectra with the overall phase set to give a maximally dispersive profile. Applying this to the rephasing spectrum gives a value proportional to the homogeneous linewidth, whereas applying it to the non-rephasing spectrum gives a value proportional to the inhomogeneous width, in the limit of strong inhomogeneity.

An alternate approach is to use the projection-slice theorem of multi-dimensional Fourier transforms. This approach had been used previously to determine the lineshapes and widths of diagonal and cross-diagonal slices in the limits of pure homogeneous broadening and strong inhomogeneous broadening. However, semiconductor quantum wells are often in the intermediate regime, where the homogeneous and inhomogeneous widths are comparable. To address this case, we extended the analysis to the intermediate regimes. A significant advantage of this approach over our previous method was the ability to fit an entire lineshape, which improves the confidence in the values.

We then used these results to analyze 2DFT spectra of the heavy-hole and light-hole exciton resonances in quantum wells broadened by weak disorder due to well width fluctuations. The analysis provided the surprising result that the light-hole resonance actually had a narrower inhomogeneous width than the heavy-hole resonance. Since both experience the same disorder landscape, at first thought, it would seem that they should have identical inhomogeneous widths. However, the difference in hole mass does change how the excitons sense the disorder. The simpler effect is simply that a lighter particle actually sees a greater change in energy for a given change in spatial confinement, which would suggest that the light-hole exciton should have a greater inhomogeneous width. However, a competing effect can arise due the fact that excitons are most sensitive to interface roughness that has spatial frequencies comparable to the inverse of the Bohr radius. Roughness that occurs on shorter length scales is averaged out. Thus we conclude that the interface roughness that occurs in the quantum wells is much stronger on length scales that correspond to the heavy hole exciton Bohr radius as compared to length scales that correspond to the light-hole exciton Bohr radius.

Another powerful capability of 2DFT spectroscopy is its ability to access coherences that are not optically active. These coherences are created in the first two pulses and then allowed to evolve during the time T. They set the initial phase of the signal emitted during time T. Thus by measuring the phase of the signal, scanning T, and taking a Fourier transform with respect to T, it is possible to observe these coherences. During the previous grant period, we had implemented this concept for measuring “Raman” coherences between the heavy-hole and light-hole exciton resonances. During the most recent grant period, we implemented it for two-quantum coherences between the ground state and two-exciton states.

Prior work had measured the magnitude spectrum for two biexcitonic two-quantum coherences. We measured the real part of the spectrum and compared it to theory. The theoretical results were able to reproduce the experimental observations, which showed dispersive resonances at the unbound two-exciton frequencies, which was reproduced in other measurements. Interestingly, the theoretical results showed that these terms appear at a mean-field level of approximation.

If GaAs quantum wells are grown to be very thin and the long growth interruptions allow the interface fluctuations to form into large, flat islands, the localized states can be energetically well separated from the delocalized states. These localized states are confined in all three spatial directions and thus have been dubbed “natural quantum dots.” The transverse localization in the plane of the quantum well is quite weak, which is a disadvantage for most applications. However, they interact strongly with light because their large physical size corresponds to a large dipole moment.

As a first demonstration of 2DFT spectroscopy of quantum dots, we chose to work on natural quantum dots because of their large dipole moment. In general, obtaining nonlinear signals from MBE grown quantum dots is challenging because they are embedded in a matrix that can give a non-resonant signal and scattering that masks the nonlinear signal. We have succeeded in obtaining clear 2DFT spectra of natural quantum dots. We studied the temperature and excitation density dependence of the homogeneous linewidth. The temperature dependence displayed an activation-like behavior, where the activation energy and coupling coefficient varied across the ensemble, both increasing for smaller dots. Extrapolating to zero temperature and excitation density yielded a linewidth that decreased for smaller dots; this was due to a reduction in radiative broadening for smaller dots because of their smaller dipole moment.

By tuning the laser to excite both the localized quantum dot states and the delocalized quantum well states, it is possible to study the transfer of excitation between them. Transfer of excitation is evident as cross-peaks that grow as T is increased. The dominant process is relaxation of quantum well states into quantum dot states; however, at elevated temperature, the reverse process begins to happen. Studying the dynamics of these peaks allowed us to develop a rate equation model that described the transfer of excitation between the various states. To get agreement with the experimental results, it was critical to include dark excitons that are formed when only one carrier (typically the hole) undergoes a spin flip. This rate equation model simply includes fixed rates for the various processes. Actually calculating these rates due to effects like phonon-carrier interactions will require a more extensive theoretical effort.

Physics of Correlated Systems

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The theory of quantum mechanics is necessary for the study fundamental physical processes at the level of atoms and molecules that control the transformations and interactions of matter and energy. As the interaction strength among atoms, molecules, and light grows stronger, it becomes extremely difficult to treat the most interesting and important systems. Our goal in this project is to develop theoretical techniques and insights, to enable more complex systems to be described by theory realistically. The set of problems considered are at the frontier of current theoretical capabilities for handling strongly-interacting or strongly-correlated systems.

This work is closely relevant to the mission of DOE because all processes involving energy control and transfer, as well as all chemical rearrangement processes, must inherently involve such correlations, which are one of the greatest difficulties for quantum mechanical approaches. Thus the progress we achieve on the set of problems proposed for study will ultimately add to our capabilities to channel energy flow as well as the rearrangement reactions associated with complex environments, and hopefully improve our knowledge about radiation damage and energy transformation. In addition to the development of theoretical techniques, another important outcome is the solution of specific theoretical problems that have not previously been cracked by applying the novel techniques introduced. Some processes of particular interest for study in this project include developing a treatment that can predict the branching ratios and angular distributions of the neutral atomic and molecular fragments in a class of dissociative recombination processes called "indirect'' or "Rydberg-dominated''. We also intend to study laser-induced control of transient absorption spectra in the vicinity of autoionizing states of atoms with two valence electrons, and more broadly, to explore intense laser-atom and laser-molecule interaction physics as well as laser-dressed electron collisions with atoms and possibly molecules.

Our recent progress has allowed us to solve new problems in the area of dissociative recombination of polyatomic molecular ions that had previously resisted solution, and we have also succeeded in describing the effect of laser-dressing of autoionizing states of the helium atom and its effect on photoionization of helium by extreme ultraviolet photons.

Strongly Anisotropic Bose and Fermi Gases

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Recent advances in slowing, trapping, and manipulating ultracold molecules have realized the ultimate limit of molecular beam experiments, by completely controlling all internal degrees of freedom as well as the relative motion of the molecules. This extraordinary technology should afford new insights into the energetics of chemical reaction dynamics. To put cold collision data to use in this way will require a comprehensive theoretical framework that elucidates what information can be had, and from which observables. The work proposed here outlines such a theory, dividing the effort into two complementary components. In the first component, the long-range interactions between molecules, including dipolar interactions, will be completely characterized by means of quantum-defect-theory (QDT) methods. These methods will relate collision observables to specific, weakly-energy-dependent information on the scattering wave function at intermediate separations R_m. In the second component, this information will in turn be exploited to understand what it can tell us about chemical reactions. Experimentally varying the long range interactions should allow experimental control over the reactants' approach to the chemical transition state, thereby revealing a wealth of chemical information. Developing a language to interpret this information is the primary goal of this proposal.

Towards Ultracold Molecules - Manipulation of Neutral, Ground-state, Free Radical OH

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A transformational change took place in the field of cold molecules over the past three years. For the first time, we have produced a gas of polar molecules in the quantum regime, with an improvement of the molecular gas phase space density by more than 11 orders of magnitude over any previous results. As a consequence, the complete control of the molecular degrees of freedom has been demonstrated, with molecules prepared in a single internal quantum state, including the nuclear spin state, and in a single collision quantum channel (partial wave) for the external motional state. Novel state-specific chemical reactions at ultralow temperatures have been discovered, revealing fundamental insights to molecular interactions. The dipolar interactions between molecules have been used to demonstrate stereo reaction dynamics in the quantum regime. Building on these dramatic advances, we will perform research on strongly confining the dipolar molecules in various spatial configurations and reduced dimensions, with the help of optical lattices. This research direction will not only provide unique realization of strongly interacting many-body quantum system with anisotropic and controllable interactions, but also open new paradigms for control of the stereo-dynamics of chemical reactions. The collective behavior of molecular interaction dynamics will be particularly fascinating to explore.

On a second experimental front where polar molecules (such as OH, ND_3, YO) are prepared at moderately low temperatures (1 mK – 1 K), we have already gained unprecedented energy resolutions for studying molecular collisions. By combining for the first time the techniques of Stark deceleration, magnetic trapping, and cryogenic buffer gas cooling, we have made the first experimental observation of cold collisions between two different species of state-selected neutral polar molecules. This has enabled an absolute measurement of the total loss cross sections between different polar molecules. Due to the dipolar interaction, the total cross section increases upon application of an external polarizing electric field. Cross sections computed from *ab initio* potential energy surfaces agree well with the measured value at zero external electric field. In the next three years, we will vigorously pursue a new technological path of laser cooling of molecules so that we will be able to bridge the energy gap between 1 μK and 1 mK. This area of research will not only complement the work in the ultralow temperatures, but also provide a unique opportunity to explore the connection between the semiclassical regime (many partial waves) and the quantum regime (single partial waves) for molecular collisions. Within this temperature range, we will need to treat only a few input collision channels. Tuning of the molecular translational energy can lead to dramatic changes in collision and reaction dynamics arising from scattering resonances that are certain to exist. One example is the resonant dipolar interaction between OH and ND_3, where we have recently developed the capability of orienting magnetically trapped OH molecules in parallel or antiparallel with the dipolar orientation of the incoming cold beam of ND_3 molecules.

Experiments in Ultracold Collisions and Ultracold Molecules

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This project is currently focused on the production of molecules at sub-millikelvin temperatures via the process of photoassociation. In the experiments, we start with ultracold Rb atoms in a magneto-optical trap and use pulses of frequency-chirped light to form excited-state molecules by long-range photoassociation of colliding atoms. These excited molecules then decay radiatively into the ground state. Nanosecond timescale manipulations of the frequency and amplitude of the pulses allow coherent control of the molecular formation process. We use state-selective ionization with a pulsed dye laser to detect the resulting ground-state molecules.

In conjunction with the molecular experiments, we are developing the technology to enable production of pulses and frequency chirps on subnanosecond time scales. Diode laser light is manipulated by fiber-optic-based electro-optical phase and intensity modulators that are driven by a fast arbitrary waveform generator. The resulting chirped pulses are 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.

Formation of Ultracold Molecules

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This research program covers interconnected topics related to the formation of ultracold molecules. During FY 2011, we made progress on four main axes of research: (1) formation of homonuclear and heteronuclear molecules, (2) Rydberg-Rydberg interactions, (3) influence of Feshbach resonances on formation rates, and (4) energy surfaces and reactions.

In (1) formation of homonuclear and heteronuclear molecules, we extended our previous work to the formation of LiH triplet molecules. These are peculiar since they support a single quantum state, a prerequisite to study degenerate molecular gases. In addition, we also explored the implication of the statistics of the components of LiH (fermions or bosons) on the chemical reaction rates when colliding with H, Li, or LiH.

In (2) Rydberg-Rydberg interactions, we investigated the interaction between two rubidium atoms in highly excited Rydberg states and show the existence of potential wells of doubly-excited atoms due to *l*-mixing. These wells are shown to be robust against small electric fields, and to support many bound states. We calculated their predissociation and show that their lifetimes are limited by the lifetime of the Rydberg atoms themselves. We also study how these vibrational levels could be populated via photoassociation, and how the signature of the ad-mixing of various *l*-character producing the potential wells becomes apparent in photoassociation spectra.

In (3) influence of Feshbach resonances on formation rates, we are extending our earlier work on Feshbach Optimized Photoassociation (FOPA) to the time-dependent regime, and we are exploring if pump-dump schemes could be employed to produce large amounts of ultracold molecules in their ground state.

In (4) energy surfaces and reactions, we are starting a new effort on reactive scattering involving cold molecules and molecular ions. We first calculated potential energy surfaces (PES) for trimers, such as for Li_3, necessary in the photoassociation of Li_2 with Li to form the Li_3. We have studied the collisions of trapped molecules with slow beams, particularly of OH molecules with ^{4}He atoms. We also calculated the structure and thermochemistry relevant to KRb+KRb collisions and reactions, and found that the K_2Rb and KRb_2 trimers have global minima at higher energies than KRb+KRb, preventing the formation of those trimers by collisions, and that K_2Rb_2 tetramers and have two stable planar structures. We have calculated the minimum energy reaction path for the reaction KRb+KRb to K_2 +Rb_2 and found it to be barrierless. Finally, we have started a new effort on molecular ions, carefully calculating their energy surface and transition dipole moments. We started with alkaline-earth elements, such as Be_2^+ dimer, since they can be cool to very low temperatures.

Algorithms for X-Ray Imaging of Single Particles

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Funding:	$150,000

A method for complete structure determination from intensity-intensity cross correlations from an ensemble of identical particles aligned along a single axis was developed and submitted for publication. This improves upon previous methods that provide only the structure projected into a plane orthogonal to the alignment axis.

Zhen Wah has started a project that grew out of discussions with Anthony Starace and Martin Centurion at the 2011 AMOS research meeting. Efforts are underway to image small molecules with ultrashort electron pulses. These researchers are simulating the experimental signals (Starace) and constructing the first experiments (Centurion). Zhen Wah will develop algorithms for reconstructing the electric potential of the molecules from their electron diffraction data.

Hyung Joo is going through a huge body of LCLS data Michael Bogan described at the AMOS research meeting and has since made available to us. This diffraction data, from individual clusters of nanoparticles, is of interest to aerosol scientists and provides an opportunity to test algorithms that will eventually reconstruct biomolecules at smaller scales.

Kartik has extended the PI's information theoretic analysis of the noise limits for reconstruction to include the effects of background scattering. This work will be submitted for publication by the end of the year. He also visited the data analysis group at LCLS and presented the simulation results he obtained with their computing cluster that demonstrated real-time reconstruction. Kartik also learned that the detector being used at the CXI end station is operating at a much higher level of electronic noise than we had assumed. When this was mentioned to Sol Gruner, whose group had developed the detector to operate at very low levels of noise (single photon detection), it was decided to carry out a mock diffraction experiment on a table-top at Cornell that tested the detector characteristics in conjunction with the algorithm we developed. The experiment is now completed and demonstrated nearly perfect reconstruction of the diffraction signal even when the signal was given an unknown rotation between frames and the mean number of photons recorded per frame was as low as three. A manuscript for publication is in preparation.

Ionization of Free and Confined Atoms and Ions

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Funding:	$70,000

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 third generation light sources, particularly ALS and APS; (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 (1) provide deeper insight into the physics of the experimental results, (2) provide guidance for future experimental investigations, and (3) seek out new phenomenology, especially in the realm of confined systems. The general areas of programmatic focus are manifestations of nondipole effects in photoionization, photoabsorption by inner and outer shells of atoms and atomic ions (positive and negative), and studies of atoms endrohedrally confined in buckyballs, C60, particularly dynamical properties. The present theoretical methodologies being used are R-matrix (both non-relativistic LS and relativistic Breit-Pauli versions), relativistic random phase approximation (RRPA), time-dependent local density approximation (TDLDA), and relativistic multi-configuration Tamm-Dancoff (MCTD) approximation, among others. Flexibility is maintained to respond to opportunities that present themselves as well.

Novel Nanoplasmonics Theory: Energy Transformation Processes at the Nanoscale in Ultrafast and Strong Laser Fields

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This program is aimed at theoretical investigations of a wide range of phenomena induced by ultrafast laser-light excitation of nanostructured or nanosize systems, in particular, metal/semiconductor/dielectric nano-composites and nano-clusters. Among the primary phenomena are processes of energy transformation, generation, transfer, and localization on the nanoscale and coherent control of such phenomena.

A major direction of research has been the prediction and study of a new phenomenon, namely Ultrafast Dynamic Metallization of Dielectric Nanofilms by Strong Single-Cycle Optical Fields. This is a dynamic metallization effect where an ultrafast (single-cycle) optical pulse with a ~1 V/Å field causes plasmonic metal-like behavior of a dielectric film with a few-nm thickness. This manifests itself in plasmonic oscillations of polarization and a significant population of the conduction band evolving on a ~1 fs time scale. These phenomena are due to a combination and mutual influence of both adiabatic (reversible) and diabatic (irreversible) pathways. Our work in this direction is actively developing in collaboration with researchers (Dr. Ferenc Krausz et al.) from Max Plank Institute for Quantum Optics (MPQ), Garching at Munich, Germany.

Among other significant advances are the following: (1) ultrafast femtosecond emission of electrons from nanoparticle induced by strong optical fields and its carrier-envelope phase control (in collaboration with MPQ) and (2) the generation of femtosecond extreme ultraviolet (XUV) pulses using nanoplasmonic enhancement via adiabatic concentration of optical energy [in collaboration with Korean Advanced Institute of Science and Technology (KAIST), Daejeon, S. Korea, and MPQ].

We continue to develop theory of ultrafast photoprocesses in metal and dielectric nanostructures in strong optical fields.

Dual Quantum Gases of Bosons: From Atomic Mixtures to Heteronuclear Molecules

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Funding: $140,000

This program centers on quantum gases of 23Na and 87Rb, 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 23Na Bose-Einstein condensate.

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 three 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.

Low-Energy Electron Interactions with Liquid Interfaces and Biological Targets

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Funding:	$145,000

The primary objectives of this program are to investigate the fundamental atomic and molecular physics involved in low-energy (5-250 eV) electron as well as ultrafast soft x-ray (20-250 eV) interactions with complex molecular targets that have biological relevance and significance. There will be a particular emphasis on understanding correlated electron interactions and energy exchange in the deep (inner) valence and shallow core regions of the collision targets. These interactions often involve ionization, Auger processes, interatomic and intermolecular Coulomb decay (ICD), and dissociative electron attachment (DEA) resonances. ICD and DEA are “local” inelastic energy-loss events which are extremely sensitive to many body effects and changes in local potentials. It is likely that both processes contribute significantly to the general damage/transformations associated with the interaction of ionizing radiation with most molecular clusters or condensed-phase “targets.” The targets we will examine range in complexity from very controlled molecular thin films to biological molecules and complicated aqueous solution interfaces. These will include (1) water clusters adsorbed on hydrophobic and weakly interacting substrates such as rare gases, multilayer hydrocarbons, and graphene; (2) nucleic acids, amino acid-nucleotide pairs, and self assembled layers of DNA and RNA; and (3) aqueous solution surfaces and interfaces containing solvated ions.

The program will be carried out mainly in the Electron- and Photon-Induced Chemistry on Surfaces (EPICS) Laboratory at the Georgia Institute of Technology (GIT) and will involve the training of a graduate student and postdoctoral fellow in a scientific discipline where atomic and molecular physics, radiation physics/chemistry and surface science converge. We have recently initiated collaborations involving the use of ultrafast x-rays at JILA, Boulder, CO. The on-going liquid beam work will be carried out at Pacific Northwest National Laboratory (PNNL). Our proposed investigations should be fruitful in extracting details regarding the roles of holes, hot electrons, and interfacial energy exchange in ionizing radiation-driven damage events. The program will also provide useful information to the community developing theories for ultrafast correlated electron dynamics and electron interactions with complex, polyatomic targets.

Theoretical Investigations of Atomic Collision Physics

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Funding:	$135,000

We have been exploring a range of atomic and molecular processes with an emphasis on collisions in cold and ultracold gases. We have continued studies of near resonance charge exchange with emphasis on the effects of non-adiabatic perturbations on collision processes governed by a strong polarization potential, and on the applicability of the prototypical two-state description of the charge exchange. The case of Be^+ in Be has been the subject of our theoretical investigation. A distinct and interesting feature arises because a third state, is involved in the collision process even at very low scattering energies. The scattering theory we have constructed leads to coupled equations of three channels. The coupling operator connects nuclear and electronic motions and is proportional to the difference in mass of the isotopes. The corresponding potential energy curves are modified in such a way that they separate at large distance to the correct energetic limits. The near resonance charge exchange cross section in the low-energy limits follows Wigner's threshold law, varying as the inverse of the initial velocity. When the collision energy is much higher than the threshold energy arising from the isotope shift, near resonance charge exchange becomes identical to resonance charge exchange.

Responding to recent experiments (J. Doyle at Harvard) on the trapping of van der Waals molecules (XHe, X=N, P, Cu, Ag, Au) in a cryogenic buffer gas, particularly for AgHe, we have explored the spin relaxation of those molecules in buffer-gas-loaded magnetic trap and identified a loss mechanism based on Landau-Zener transition arising from the anisotropic hyperfine interaction. We have used ab initio calculations of the interaction potentials and hyperfine interactions, quantum collision calculations and Monte Carlo trap simulations to compare our model with experiment. We found close quantitative agreement, providing indirect evidence for molecule formation in a buffer-gas trap. The formation of AgHe goes through a three-body collision process..

We have continued our research on the thermalization of an initially energetic parcel of gas traversing a uniform bath gas and extended from the case of atom-atom collisions to the atom-diatom collisions, specifically, $O+H_2$. We have applied our theory and numerical algorithm in applications of planetary atmospheric science. We have proposed and evaluated a He escape mechanism from the Martian atmosphere due to collisions with hot O(1D,3P). Our predicted rate of escape agrees closely with the data derived from the observation.

Ultracold Molecules: Physics in the Quantum Regime

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Our research encompasses a unified approach to the trapping of diverse chemical species of both atoms and molecules and the study of their collisions. Our current goal is to magnetically trap CaH. This will be done by taking molecules from our newly developed slow beam source, with velocity of about 50 m/s, and optically pump them into a deep magnetic trap. We have assembled the necessary lasers for driving the transitions and for detection, as well as configured our superconducting magnetic trap in its cryostat. Half of the overall vacuum chamber is constructed.

Our immediate plans are to finish the construction of the vacuum chamber, and test our magnetic trap (by bringing it up to full current). Next, we will run our cold molecular beam and detect CaH molecules in the beam, just before they enter the trap. We hope that by some time next calendar year we will optically pump the molecules into the trap. We are also continuing development on improved sources for our molecule, CaH.

Atomic and Molecular Physics in Strong Fields

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Funding:	$105,000

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

Examples of more specific topics currently being explored include (a) probing the origin of elliptical high-order harmonic generation from aligned molecules in linearly polarized laser field, (b) accurate treatment of above-threshold-ionization spectra from core region of time-dependent wave packet: a new ab initio time-dependent approach, (c) high precision study of the orientation effects in MPI/HHG of H_2^+ in intense laser fields, (d) exploration of the role of the electronic structure and multi-electron response in the MPI and HHG processes of diatomic molecules in intense laser fields, and (e) theoretical study of orientation-dependent MPI of small polyatomic molecules in intense ultrashort laser fields: a new time-dependent voronoi-cell finite difference method.

PULSAR: A High-Repetition-Rate, High-power, CE Phase-Locked Laser for the J.R. Macdonald Laboratory

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Funding:	$1,274,000

The J.R. Macdonald Laboratory is in the process of installing a new cutting edge "High repetition rate, high power, carrier-envelope phase -locked laser.” The main laser system was purchased from KMLabs while pulse compression and characterization systems are built in house. We expect the laser to be operational by the end of the year and implement it for our studies of the interaction of intense laser pulses with matter – specifically, observing and controlling single atoms and molecules on short time scales. The eventual goal is to work at the natural time scale for electrons moving in matter. Doing so will add to our existing capability to trace nuclear motion in molecules using femtosecond laser pulses. All of these activities build toward the ultimate goal of understanding the dynamical processes of reactions well enough to control them. To this end, we are advancing theoretical modeling and computational approaches as well as experimental techniques and taking advantage of our expertise in particle imaging techniques (such as COLTRIMS, VMI, MDI, etc.). Most of our research projects are associated with one of the two themes: “Attosecond Physics” and “Control.”

Structure and Dynamics of Atomics, Ions, Molecules and Surfaces

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Funding: $2,500,000

The J.R. Macdonald Laboratory focuses on the interaction of intense laser pulses with matter – specifically, observing and controlling single atoms and molecules on short time scales. The eventual goal is to work at the natural time scale for electrons moving in matter. Doing so will add to our existing capability to trace nuclear motion in molecules using femtosecond laser pulses. All of these activities build toward the ultimate goal of understanding the dynamical processes of reactions well enough to control them. To this end, we are advancing theoretical modeling and computational approaches as well as experimental techniques and taking advantage of our expertise in particle imaging techniques (such as COLTRIMS, VMI, MDI, etc.). Most of our research projects are associated with one of the two themes: “Attosecond Physics” and “Control.” The boundary between these themes, however, is sometimes not well defined.

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

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Funding: $145,000

In this project, we aim at achieving time-resolved imaging of a molecule with sub-Angstrom spatial resolution using intense ultrafast infrared (IR) or near-infrared (NIR) lasers. When a molecule is exposed to an intense laser field, electrons that are removed in the early stage of the pulse may be driven back to recollide with their parent ions. The recolliding electrons may recombine with the ion to emit high-order harmonics or may scatter elastically from the ion. In both processes, information about the target ion at the time of collisions is imbedded in the photon or electron spectra. Since IR and NIR lasers with durations of a few femtoseconds are already available, if the target structure can be retrieved from the photon and electron spectra, then sub-Angstrom spatial resolution with few-femtosecond temporal resolution can be achieved. Our project aims to provide the theoretical foundation such that structural information can be retrieved from the experimental data. In fact, we have already shown that the bond length of oxygen molecule shrinks by 0.1 Angstrom in about 5 fs after its outermost electron is removed. We also have been able to show that our theory can now predict the measured photon spectra from simple molecules. Extending the theory to more complex molecules is underway.

Resonant and Nonresonant Vibrational Effects in the Photoionization Dynamics of Asymmetric Systems

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We study how photoelectrons interact with anisotropic molecular frameworks in a variety of contexts, including molecular photoionization and high field ionization. Such investigations illuminate new types of spectroscopy, and address the Grand Challenge issues of central importance to the DOE mission. In the simplest view of molecular photoionization, one assumes that vibrational and photoelectron motion are decoupled, which leads to the Franck-Condon approximation. The Franck-Condon principle has two predictions that are relevant to molecular ionization: (1) vibrational branching ratios are independent of photon energy, and (2) single quantum excitations of nontotally symmetric modes are forbidden. Nonresonant and resonant processes can result in coupling molecular vibration and photoelectron motion, with the result that vibrational branching ratios become dependent on photon energy, and that forbidden vibrations can be excited. We have studied a variety of systems that extend our understanding of such photoelectron/vibrational coupling, such as halothiophenes.

Experimentally, we have made considerable progress on these systems. We have identified many vibrational excitations that exhibit non-Franck-Condon behavior at low photon energies.There also appears to be deviations at higher photon energies. In addition to the resonant studies, we have extended our investigations to explore nonresonant photoelectron/vibrational couplings in cyanogen halide molecules XCN (X = Cl, Br, I). Non-Franck-Condon behavior arises from charge transfer effects in the initial states, and these are new effects that have not been anticipated or observed previously. Finally, we have analyzed the the momentum distributions of rescattering photoelectrons generated by infrared laser pulses. The extracted DCSs are in good agreement with our computed ab initio results, confirming the validity of the extraction procedure. Noting that the double-slit-type interference includes information about the distances between the atoms of a molecule, the results of this study has a further implication that the rescattering electron spectroscopy is indeed potentially a powerful tool for determining the structure of molecules and thus may be employed for studying chemical reactions with a temporal resolution of femto- or subfemtoseconds and with atomic spatial resolution. All of these research directions highlight the utility of probing fundamental aspects of the anisotropic molecular potential that is intrinsic to studies of continuum photoionization problems.

Condensed Matter Spectroscopy on Ultrafast Time Scales and Mesoscopic Length Scales

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Funding:	$145,000

This project is aimed at direct spectroscopic characterization of phenomena that occur on mesoscopic (nanometer) length scales and ultrafast time scales in condensed matter, including non-diffusive thermal transport and the high-wavevector acoustic phonon propagation that mediates it, complex structural relaxation and the density and shear dynamics that mediate it, and nanostructure thermoelastic responses. A primary effort in the project is directed toward nonlinear time-resolved spectroscopy with coherent soft x-ray, or extreme ultraviolet (EUV), wavelengths. Time-resolved transient grating (TG) measurements are conducted in order to directly define an experimental length scale as the interference fringe spacing formed by two crossed excitation pulses or by a fabricated spatially periodic pattern that is irradiated by a single excitation pulse. The dynamics of material responses at the selected wavevector, including thermoelastically induced surface acoustic waves and thermal diffusion or non-diffusive thermal transport, are recorded through time-resolved measurement of coherent scattering (i.e., diffraction) of variably delayed probe pulses from the transient grating pattern. Progress in high harmonic generation has yielded femtosecond EUV pulses with sufficient energy and focusability for use in TG experiments. EUV probe pulses provide far greater sensitivity than optical pulses to surface acoustic and thermal responses, since the surface modulations change the EUV phase by far more than the optical phase and thereby yield far higher EUV diffraction efficiencies. Crossed EUV excitation pulses will produce interference fringe spacings of tens of nanometers, far smaller than is possible with crossed optical pulses, providing access to mesoscopic length scales, very high acoustic frequencies, and non-ballistic thermal transport.

In complementary measurements, the frequency rather than the wavevector of an acoustic response is specified by using a sequence of femtosecond excitation pulses at a specified repetition rate, with each pulse thermoelastically driving a single acoustic cycle. In this case, the acoustic wave propagates through the sample rather than along the surface and detection is carried out at the opposite sample surface, i.e., multiple-pulsed excitation is at the front and detection is at the back of the sample. This approach provides access to high-frequency bulk acoustic waves, while the EUV measurements are used to examine surface acoustic waves. Bulk longitudinal and transverse waves can be excited monitored. GHz-frequency shear waves can be observed in viscous fluids whose structural relaxation dynamics occur on nanosecond or slower times scales, permitting study of supercooled liquids and the liquid-glass transition. The phononmean free paths can be measured to provide insight into diffusive and non-diffusive dynamics of phonon-mediated thermal transport.

Understanding and Controlling Strong-Field Laser Interactions with Polyatomic Molecules

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The objective of our research is to first unravel the contributions from both coherent and incoherent processes taking place when intense near-IR pulses interact with polyatomic molecules, and then to use this knowledge to develop robust strategies for controlling laser-matter interactions so that order-of magnitude changes in the branching ratios of these photochemical processes can be realized.

APPROACHES

(a) In order to determine the role of electronic coherence we devised a new method to synthesize intense non-interfering pulse replica. Because this is a radically new approach we tested it on a large fluorescent molecule in solution. The findings confirm the validity of our approach, and demonstrate that this method does not impose on the molecular system the inherent interference between pulses of standard interferometric methods. This work is being prepared for publication. Further refinement of the method reveals early wavepacket dynamics that are related to those observed with chirped pulses. Experiments comparing fluorescence and stimulated emission reveal the processes are out-of-phase and show early wave packet dynamics that are also associated with the Stokes shift in fluorescence. These findings are being prepared for publication.

(b) The approach above has been used to study the lifetime of electronic coherence as it exists following the interaction of an intense near-IR pulse and a polyatomic molecule. Our findings confirm our earlier observations that the electronic coherence is short lived, in most fragments lasting less than 50fs. These findings are being prepared for publication.

(c) We are completing the construction of a photoelectron photoion coincidence (PEPICO) instrument that we will use to further unravel the behavior of polyatomic molecules under intense fields.

Dynamics of Few-Body Atomic Processes

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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 (including electron correlations) 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. The current project involves theoretical investigations of electronic processes in atoms that make use of near-future experimental capabilities.

Our investigations fall into three broad areas: (1) few-cycle attosecond pulse ionization processes in the nonlinear regime, (2) multiphoton ionization processes in the extreme ultraviolet (XUV) regime, and (3) electron correlation effects on intense laser-atom processes, such as high-order harmonic generation. Nearly all proposed projects require large-scale numerical computations, involving, e.g., the direct solution of the full-dimensional time-dependent or time-independent Schrödinger equation for two-electron (or multi-electron) systems interacting with electromagnetic radiation. Principal benefits and outcomes of this research are improved understanding of how to control atomic processes with electromagnetic radiation, how to transfer energy from electromagnetic radiation to matter, and how to image electron correlation processes while they occur.

Early Career - Ultrafast Electron Diffraction from Aligned Molecules

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Funding:	$150,000

This project will implement a new method to capture the 3D structure and dynamics of molecules with atomic resolution. 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 1-D 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. Using a short laser pulse, it is possible to create a distribution of molecules that are aligned a short time after interacting with the laser pulse. This creates a field-free sample of molecules that can be studied. The idea consists of recording multiple electron diffraction patterns by rotating the alignment axis, each one corresponding to a different projection of the molecule. A 3D image of the structure can be retrieved by merging the information from multiple diffraction patterns.

Laser Produced Coherent X-Ray Sources

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Funding:	$150,000

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.

A promising approach to the development of a compact source of ultrashort-pulse-duration x-rays is one that employs Thomson scattering of intense laser light from a relativistic electron beam. In this process, 1-eV energy laser light can be Doppler-shifted (by a factor of up to 106). Measurements with such a photon source could provide information on the structure of matter with atomic-scale resolution, on both the spatial and temporal scale lengths–simultaneously. Moreover, because the electron beam is accelerated by the ultra-high gradient of a laser-driven wakefield – via a light pulse from the same laser system that produces the scattering pulse– the combined length of both the accelerator and wiggler regions is only a few millimeters.

The work in this project is concerned with the development of high-brightness, compact x-ray sources and their applications. This will be enabled by our recently demonstrated capability to produce monoenergetic electron beams in a reliable way. These beams have an angular divergence of a few mrad, an energy spread <10% and 400-600 pC of charge. The use of a stable well-characterized laser system leads to a stable accelerator. We will extend our preliminary work already performed on x-ray generation to perform the following major activities:

- Quasi-monoenergetic x-ray beams via Thomson scattering.
- Polychromatic x-ray beams from betatron oscillations in a plasma channel.
- Development of a source suitable for ultrafast electron diffraction.
- Expansion of beamline to include electron and x-ray diagnostics.
- Demonstration of applications of the source in proof-of-concept experiments.
- Demonstration of the ultrafast nature of the x-ray and electron source in independent measurements.

We will further improve the quality of the ultrafast x-rays, minimize their pulse duration, and apply them to the study real-time ultrafast dynamics. These sources are expected to produce 108-109 photons/sec in the energy range 1-100 keV in a 10% bandwidth with pulse duration ~30 fs, enabling the study of ultrafast structural dynamics by use of diffraction with femtosecond resolution. The development of such sources involves physics at the forefront of relativistic plasma physics and beams, as well as relativistic nonlinear optics. Applications include the study of ultrafast chemical, biological and physical processes, such as inner-shell electronic or phase transitions, pump-probe measurements of photo/impact ionization of atoms and molecules, nonthermal melting of solids, as well as the study of shocks in high-density materials.

Energetic Photon and Electron Interactions with Positive Ions

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Funding: $165,000

This experimental program addresses fundamental interactions of extreme ultraviolet light with atomic and molecular ions. The principal investigator developed and operates a multi-user merged ion-photon-beam research endstation at the Advanced Light Source (ALS) designed to use monochromatized synchrotron radiation to probe photoionization of positive ions. The high photon beam intensity and energy resolution at ALS undulator beamline 10.0.1.2 enable 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. Another current emphasis is photoionization of so-called endohedral fullerene (or endofullerene) molecular ions, in which an atom is confined within the fullerene cage. Such molecules have promising practical applications in energy research, quantum computing and medicine.

Confinement resonances associated with the interaction of energetic photons with such “caged atoms” are predicted by numerous theoretical studies. The effect is attributed to interference between direct photoelectron waves from the caged atom and waves scattered by the cage. Considerable disagreement exists concerning their relative phase and amplitude, and even concerning their existence. A noble gas atom such as xenon does not form ionic bonds and should be centered within a fullerene molecular cage. Xenon also exhibits a "giant resonance" in inner-shell photoexcitation 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, apparatus was developed to synthesize them directly in the laboratory, both on-line and off-line of the photoionization experiments. Initial measurements with caged xenon are strongly suggestive of the predicted confinement resonances. A current objective is to refine these measurements and their statistical precision as higher-yield endofullerene materials are synthesized. 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 are under way with both fullerene and endofullerene molecular ions to probe the underlying mechanisms in more detail.

Combining High Level Ab Initio Calculations With Laser Control of Molecular Dynamics

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Funding:	$120,000

This project is focused on developing methods to probe and control molecular dynamics through conical intersections. Close collaboration between theory and experiment is a major element of this project in which high level ab initio electronic structure calculations are combined with experiments using shaped ultrafast laser pulses. The calculations help guide and interpret the control and the time resolved spectroscopy experiments. The experiments help test calculations, yield information about dynamics, and can demonstrate control in cases where the calculations give promise. Specific objectives in this project include (1) the development of strong field dissociative ionization pump-probe spectroscopy to probe the relaxation dynamics of molecules excited in the deep UV; (2) the development of pulse shape spectroscopy, where molecular relaxation dynamics are studied as a function of pump pulse shape; and (3) the implementation of multi-parameter, closed loop learning control of molecular relaxation through competing pathways from an excited state to the ground state via conical intersections.

In our previous work we developed a new approach for studying radiationless relaxation in molecules after excitation to an electronically excited state. A strong field infrared probe pulse ionizes and fragments the molecule as it evolves on the excited state following absorption of a UV pump pulse. Different molecular fragments measured with time of flight spectroscopy and identified with the help of our ab initio calculations can be used to track the wave packet on the excited state at different locations, giving us a unique picture of the molecular relaxation dynamics not possible in traditional approaches. Excited state dynamics are often controlled by conical intersections (CIs), making probing dynamics through conical intersections a focus of our work. We have demonstrated this approach on the DNA base cytosine and we are interested in applying it to the other DNA and RNA bases. Every base has a somewhat different mechanism with different pathways involved, providing several interesting cases of CI-facilitated excited state dynamics, for which our approach is well suited to study.

We are working towards the development of pulse shape spectroscopy, where molecular relaxation dynamics are studied as a function of pump pulse shape. We have begun performing 2D Fourier transform spectroscopy using shaped ultrafast laser pulses in the deep UV and we will extend this to multidimensional spectroscopies with shaped laser pulses. In addition to experiments where we study the molecular relaxation dynamics as a function of a specific pulse shape parameterization, we are also implementing closed loop control experiments which aim to select between multiple relaxation pathways. Fragments associated with a specific relaxation pathway are used as a feedback signal and the relaxation dynamics for optimal pulses are studied in pump-probe experiments.

New Directions in Intense Laser Alignment

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Funding:	$110,000

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 previous DOE-supported research in this area has successfully extended the concept of nonadiabatic 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. Although part of this research has been continued during the past year and aimed at the extension of alignment from the domain of physics and optics to make a tool in material science, solution chemistry, and possibly engineering, our main effort in 2011 has been devoted to the problem of high harmonic generation (HHG) from aligned molecules. This research 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 colleagues.

Our work on methodology development and applications in the area of HHG from aligned molecules is discussed in sections 1 and 2 below. Our work on laser alignment in complex materials is discussed in sections 3 and 4. Section 5 summarizes briefly our recent and ongoing work on the role of alignment in laser filamentation.

(1) EXTRACTING ELECTRON DYNAMICS FROM EXPERIMENTAL HIGH HARMONIC SIGNALS

In recent and ongoing work in collaborations with AMOS colleagues Murnane and Kapteyn, we combine high quality HHG experimental signals with our previously developed exact theory of high harmonics from aligned molecules to extract the fundamental electronic dipole elements that embody the complex electron dynamics giving rise to HHG. Our analysis points to a previously unexplored process in HHG, wherein the continuum electronic wavepacket gains angular momentum from the photon field to recombine at a higher angular momentum state than that with which it is ejected into the continuum. Such electron angular momentum non-conserving events dominate over angular momentum conserving processes for both CO_2 and N_2O, increasingly so as the harmonic order grows. Interestingly, the combination of theory with experimental data indicates that only a few electron partial waves contribute to the HHG dynamics. We showed also that the high-order nature and structural sensitivity of HHG make it particularly attractive as a means of studying rotational coherences. Although this was demonstrated in our theoretical work before, the present work is the first to substantiate this argument with sufficiently high-accuracy data. A joint publication was submitted to *Physical Review Letters*.

(2) SIGNATURES OF THE MOLECULAR POTENTIAL IN THE ELLIPTICITY OF HIGH-ORDER HARMONICS FROM ALIGNED MOLECULES

In recent work, we explore the information content of the polarization of high-order harmonics emitted from aligned molecules driven by a linearly polarized field. The study builds upon our recent publication, which illustrated the origin of ellipticity in HHG from linear molecules driven by linearly polarized fields, thus resolving a longstanding controversy in the experimental literature. We use a simple model potential and systematically vary the potential parameters to investigate the sense in which, and the degree to which, the shape of the molecular potential is imprinted onto the polarization of the emitted harmonics. Strong ellipticity is observed over a wide range of potential parameters, suggesting that the emission of elliptically polarized harmonics is a general phenomenon, yet qualitatively determined by the molecular properties. The sensitivity of the ellipticity to the model parameters invites the use of ellipticity measurements as a probe of the continuum wavefunction and the underlying molecular potential. An article was published as a Rapid Communication in *Physical Review A*.

(3) MOLECULAR FOCUSING AND ALIGNMENT WITH PLASMON FIELDS

In a recent publication, we show the possibility of simultaneously aligning molecules and focusing their center-of-mass motion near a metal nanoparticle in the field intensity gradient created by the surface plasmon enhancement of incident light. The rotational motion is described quantum mechanically while the translation is treated classically. The effects of the nanoparticle shape on the alignment and focusing are explored. Sharp molecular focusing occurs in the plasmon-enhanced fields for all nanoparticle shapes. Our results suggest the potential application of metal nanoparticles and their arrays to create molecular nanopatterns with orientational and spatial order that are both subject to control. These results also invite the extension of our approach to trap atoms or ions in the plasmon-enhanced inhomogeneous field, with potential applications in logic and lithography. An article appeared in *NanoLetters*.

(4) COHERENT TORSIONAL ALIGNMENT

In a recent study we extend the concept of nonadiabatic laser alignment to address the case of nonrigid polyatomics. Specifically, we propose a coherent, strong-field approach to control the torsional modes of polyatomic molecules, and develop a numerical method to simulate the torsional dynamics. By choice of the field parameters, the method can be applied either to fix the torsion angle to an arbitrary configuration or to induce free internal rotation in a predetermined sense. Transient absorption spectroscopy is suggested as a general probe of torsional control and the usefulness of this approach is numerically explored. Several consequences of our ability to manipulate molecular torsional motions are illustrated. These include a method for the inversion of molecular chirality and an ultrafast chiral switch. An article is in press in the *Journal of Chemical Physics*.

(5) THE ROLE OF NONADIABATIC ALIGNMENT IN LASER FILAMENTATION

In recent studies, we combine short-pulse pump-probe experiments with alignment and rotational revivals calculations to explore fundamental processes in laser filamentation in air. Specifically, we study the fluorescence intensities from two bands as a function of the pump-probe time delay. Our experimental and numerical results are interpreted in terms of a universal phenomenon of population trapping of nitrogen molecules in highly excited states. Along with field induced alignment and rotational revivals of the nitrogen molecules, the population trapping gives rise to enhancement and periodic modulation of the signal, which are fully explained by our theory. Our results carry important implications to the prospect of remote sensing. An article appeared in *Journal of Physics B,* and a review appeared in *Laser Physics*.

Attosecond and Ultra-Fast X-Ray Science

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Funding: $200,000

The potential for broad science impact of ultra-fast ($< 10^{-12}$ s), short wavelength radiation (< 10 nm) was recognized by the 1999 Basic Energy Sciences Advisory Committee report titled, “Novel Coherent Light Sources.” These 4th generation light sources encompass schemes that utilized both table-top and accelerator-based methods. This renewal proposes to explore two 4th generation schemes for enabling time-resolved science using ultra-fast short wavelength light pulses. In one continuing thrust, light pulses of extraordinary brevity (atomic unit of time = 25×10^{-18} s = 25 attoseconds) have been developed and applied to probe the real-time motion of complex electron dynamics. In a second thrust, x-rays of unprecedented peak power available at the Linac Coherent Light Source (LCLS) X-ray Free-Electron Laser (XFEL) at the Stanford Linear Accelerator Center will open unique opportunity for studying novel states of matter.

The new frontier of attophysics aims at visualizing and controlling in real time the motion of electrons composing matter. In the new millennium the generation of attosecond XUV pulses became a laboratory reality. A primary goal of this renewal is to apply these light pulses in a series of time-resolved experiments in order to understand correlated electron dynamics, and by doing so provide a new perspective on elementary atomic processes. These studies will be enabled by the unique technology developed at OSU for attosecond science and includes the newly constructed OSU attosecond beamline/end-station. Many of the key technological milestones were achieved in the previous grant cycle and provide a firm foundation for continued progress in the renewal. A second thrust will continue to push the cutting edge in generating shorter, brighter and more energetic attosecond bursts using long wavelength fundamental fields.

The second scope of this proposal is the continued implementation of AMO science program using the ultra-fast, intense x-rays available at LCLS XFEL. The objective is the study of fundamental atomic processes involving multiple inner-shell ionization, x-ray nonlinear optics and the development of unique methods for time-resolved x-ray physics. These investigations will also enable novel metrological methods for the characterization of the LCLS beam and the foundation for understanding more complex matter-x-ray interactions (e.g., biological imaging).

In addition, this proposal will allow the development of experimental and intellectual competency using different fourth generation platforms whether on laboratory attosecond sources or the larger facilities available at the LCLS. The OSU group has already trained graduate students and post-doctoral research associates that are now contributing to x-ray science as staff members at DOE laboratories.

Imaging of Electronic Wave Functions During Chemical Reactions

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Funding:	$222,000

Understanding chemistry at its most fundamental level requires the ability to visualize the electrons that form chemical bonds and ultimately the capacity to control the creation and destruction of these bonds. The ability to “clock” the nuclear dynamics of reactant molecules through the transition state and the evolution of product molecules on the 10-100's femtosecond (10^{-15} s) time-scale was developed in the latter part of the 20th Century as documented by the 1999 Chemistry Nobel Prize given for “femtochemistry.”

However, mechanistic organic chemistry begins with the movement of electrons with respect to the (nuclear) structure of the molecule. Once the electrons move the nuclei adjust along the resulting potential energy surface causing the nuclear dynamics, i.e., chemical reaction, to occur. Experimentally clocking and imaging these initial electron “movements” is an unmet challenge in chemistry. In 2007 a DOE/BES report titled, “Directing Matter and Energy: Five Challenges for Science and the Imagination” identified this problem as one of the five Grand Challenges for advancing the future of energy research.

In this grant an experimental program is described that is designed to meet the challenge of “watching and clocking” the electron motion during chemical bond breaking. The program is built on two seminal technical advances in the new millennia. The first is the realization of attosecond (10-18 s) burst of XUV light (the electronic “clock”) and the second is a method of tomographic imaging of the molecular wave function (the detector to “watch”). We are pursuing a novel approach of combining these techniques using mid infrared radiation to satisfy the conditions necessary for tomographic imaging of open-shell chemically reactive molecules. These techniques allow us to exploit fundamental principles of strong-field scaling and lead us down the road to electronic imaging in chemistry and materials processes.

Control of Molecular Dynamics: Algorithms for Design and Implementation

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Funding:	$130,000

This research is concerned with the theoretical and algorithmic developments addressing control over quantum dynamics phenomena, with a particular focus towards exploring basic principles of importance for laboratory studies. Several projects, involving two graduate students and one undergraduate student, have been pursued during FY 2011, and the results are summarized below.

(1) Attaining persistent field-free control of open and closed quantum systems. An assessment of the feasibility of achieving persistent quantum control (PQC) for arbitrary finite-level systems and observables has been given. The theoretical estimates of PQC behavior has been encouraging and suggested feasible exploration in the laboratory using currently available technology.

(2) Exploring the top and bottom of the quantum control landscape. The landscape for the transition probability between the states of a finite level quantum system has been considered. Level sets of controls that produce the same transition probability value are shown to exist at the bottom and top of the landscape with the field and/or Hamiltonian structure as controls.

(3) Optimal laser control of molecular photoassociation. Simulations have been performed for the electronic ground-state collision of O + H, with the goal to drive the transition from the colliding atoms to the vibrational ground level of the diatomic molecule. Very high yields have been obtained in the molecular vibrational ground level.

(4) Monotonically convergent algorithms in quantum dynamical control. A general method has been introduced to formulate monotonically convergent algorithms for identifying optimal control fields to manipulate quantum dynamics phenomena beyond the linear dipole interaction.

(5) Search complexity and resource scaling for the quantum optimal control of unitary transformations. New methods have been developed for quantifying Hamiltonian-dependent and kinematic effects on control optimization of arbitrary unitary transformations. The feasibility of performing such optimizations has been determined, particularly, for systems with large Hilbert spaces.

(6) Fidelity between unitary operators and the generation of robust gates against off-resonance perturbations. A functional expansion of the fidelity between two unitary matrices has been given in order to find necessary conditions for the robust implementation of a target gate. By exploiting techniques from robust design optimization, we have accounted for issues of experimental feasibility by introducing an additional criterion to the search for control pulses.

Antenna-Coupled Light-Matter Interactions

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We study light-matter interactions in nanoscale environments. More use ’optical antennas 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 photodetection, light emission, sensing, heat transfer, and spectroscopy.

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) 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 exploring the possibility of antenna-coupled electro-optical transduction, i.e., processes in which electrons are locally converted into photons and vice vera. We are studying optical rectification at metal-metal tunneling junctions to directly convert incident photons to electrons (optical rectennas) and electron-plasmon coupling to convert tunneling electrons to photons.

Atomic Electrons in Strong Radiation Fields

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Funding:	$100,000

Our goal is to improve theoretical understanding of the way very intense laser light interacts with and partially controls atoms and molecules, in connection with national and international experimental work in the same domain. Our study is attacking 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 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, keeping track of all sources of correlation.

Our work builds on numerically modeled experiments on atoms with two, three, and four active electrons in strong time-dependent and phase-coherent fields. To do this, we use very large ensembles (1M - 10M members) of classical multi-electron trajectories, a technique uniquely capable of non-perturbative multi-electron results for arbitrary ellipticity. It has achieved what we believe is the only direct comparison of ion-momentum distribution data between theory and experiment in triple ionization, and the explanation for unexpected transverse ion-momentum peaks that are observed in laboratory work.

Examples of topics where we expect future work to be successful are (1) multiple-electron ionization, (2) effects arising from finite ellipticity of the laser field or fields, (3) observation of breakdown of the single-active electron (SAE) approximation, and (4) demonstration of correlation via multi-electron pre-ionization joint-memory.

Combining High Level Ab Initio Calculations With Laser Control of Molecular Dynamics

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Funding:	$100,000

This proposal aims at developing methods to probe and control molecular dynamics through conical intersections. Close collaboration between theory and experiment is the major element in this proposal where high level ab initio electronic structure calculations are combined with experiments using shaped ultrafast laser pulses. The calculations help guide and interpret the control and the time resolved spectroscopy experiments. The experiments can help test calculations, yield information about dynamics, and demonstrate control in cases where the calculations give promise. Specific objectives in this proposal include (1) strong field dissociative ionization pump-probe spectroscopy to probe the relaxation dynamics of molecules excited in the deep UV, (2) the development of pulse shape spectroscopy where molecular relaxation dynamics are studied as a function of pump pulse shape, and (3) multiparameter, closed loop learning control of molecular relaxation through competing pathways from an excited state to the ground state via conical intersections.

In our previous work we have developed a new approach for studying molecular radiationless relaxation in molecules after excitation to an electronically excited state. A strong field infrared probe pulse ionizes and fragments the molecule as it evolves on the excited state following absorption of a UV pump pulse. Different molecular fragments measured with time of flight spectroscopy and identified with the help of our ab initio calculations can be used to track the wave packet on the excited state at different locations, giving us a unique picture of the molecular relaxation dynamics not possible in traditional approaches. Excited state dynamics are often controlled by conical intersections, and thus probing dynamics through conical intersections is a focus of our work. We have demonstrated this approach on the DNA base cytosine and we are interested in applying it to the other DNA and RNA bases. Every base has a somewhat different mechanism with different pathways involved, providing several interesting cases of CI-facilitated excited state dynamics, for which our approach is well suited to study.

We will work towards the development of pulse shape spectroscopy where molecular relaxation dynamics are studied as a function of pump pulse shape. We have begun performing 2D Fourier transform spectroscopy using shaped ultrafast laser pulses in the deep UV, and we plan on extending this.

We are developing tools for discriminating between different relaxation pathways and there are multiple indications that the relaxation dynamics are sensitive to the initial wavepacket launched on the excited state surface. In cases where there are multiple pathways we are interested in trying to control which relaxation pathway is taken. In cases where a single conical intersection seam is involved we want to be able to control how branching through a CI occurs. We will use closed loop control to achieve control in these cases.

High Intensity Femtosecond XUV Pulse Interactions with Atomic Clusters

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The nature of the interactions between high intensity, ultrafast, near infrared laser pulses and atomic clusters of a few hundred to a few thousand atoms have been well studied by a number of groups world wide. Such studies have found that these interactions are more energetic than interactions with either single atoms or solid density plasmas, and that clusters explode with substantial energy when irradiated by an intense laser. Under the previous phase of BES funding we extended investigation in this interesting avenue of high field interactions by undertaking a study of the interactions of intense extreme ultraviolet (XUV) pulses with atomic clusters and, more recently, a study of interactions with intense x-ray pulses from the Linac Coherent Light Source (LCLS). Our current work, funded under our recently renewed grant, builds on our previous work with a high energy high harmonic (HHG) femtosecond XUV source and seeks to study these XUV/cluster interactions at two to three orders of magnitude higher XUV intensity than we obtained in the laser phase. This is being accomplished by upgrading our HHG beam line to much higher drive energies on our new THOR Petawatt laser.

The goal of our experimental program has been to extend experiments on the explosion of clusters irradiated at 800 nm to the short wavelength regime (1 to 50 nm). The clusters studied range from a few hundred to a few hundred thousand atoms per cluster (i.e., diameters of 1-30 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. Most of our previous studies have been conducted with an XUV source created by converting a high-energy (0.1 J) femtosecond laser to the short wavelength region through high order harmonic generation in a gas jet. Soon we will be able to generate short wavelength pulses with up to 30 J of laser drive energy in a much longer focal length geometry than previously employed.

Our main interest with this upgraded HHG beam line is to continue experiments in Ar and Xe clusters augmented by experiments in solid material clusters of a range of low- to high Z materials. 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. The other major aspect of our new work is an exploration of the transition of explosions in these XUV irradiated clusters from hydrodynamic expansion to Coulomb explosion. Initial experiments on the THOR HHG beamline at 38 nm suggested that Xe and Ar clusters exhibited different explosion mechanisms. The work we intend with the upgraded HHG beam line will explore clusters of a range of atoms, including clusters from van der Waals bonded gas atoms and molecules (Xe, Kr, Ar, Ne, N_2,and CH_4) as well as clusters from solids (e.g., SiO_2 and SnO_2). Experiments on clusters from solids will be enabled by development during the past grant period in which we constructed and tested a cluster generator based on the Laser Ablation of Microparticles (LAM) method. Using a LAM device we will explore oxide clusters as well as metal clusters chosen such that the intense XUV pulse rests at a wavelength that coincides with the giant plasma resonance of the metallic cluster.

Studies of Autoionizing States Relevant to Dielectronic Recombination

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Funding:	$148,000

During the past year we have worked on two topics. The first is optical excitation in the presence of the microwave field. When an atom is exposed to laser photons more energetic than the ionization limit a photoelectron is produced which quickly leaves the ion core. If, however, a microwave field is present the electron can remain bound in the combined atom-microwave field system. We have developed a simple classical model to show that the electron remains bound if the laser excitation occurs at the phase of the microwave field such that it removes energy from the photoelectron. The phase is p/6 after the positive going zero crossing of the field. In the past year we have shown this model to be correct by photoionizing the atoms with a ps laser pulse at a controllable phase of the microwave field and detecting the bound atoms as a function of the phase at which the excitation occurs.

According to the model, just as excitation at the correct phase of the microwave field leads to removal energy from the photoelectron, in the case of excitation at the phase p/6+p the microwave field gives energy to the photoelectron. To test this prediction we have produced bound wave packets with the ps laser pulse in the presence of the microwave field and analyzed the resulting final states by selective field ionization. As predicted, we see microwave phase dependent increases and decreases in the final state energy, indicating the phase dependent absorption of energy from and loss of energy to the microwave field. We are presently finishing the analysis of these data and preparing a report of this work.

The second topic we have explored is autoionization in weak electric fields. Creating a well defined Stark state in any atom other than hydrogen usually requires a substantial, ~1000 V/cm, electric field, which precludes the use of well characterized small, ~10 V/cm, fields. We have circumvented the high field problem by using a microwave Stark switching approach which enables us to produce Stark states at very low fields of 0-20 V/cm. We have used this technique to make low field bound Stark states from which we have explored the optical spectroscopy of the autoionizing Ba 6p1/2nk Stark states in very low electric fields, where the Stark shifts are comparable to the autoionization rates of the 6p1/2ng states, and the higher l states have autoionization rates far less than the 6p1/2ng states and often less than 1 GHz. Using the microwave Stark switching technique we can produce 6snl states of l = 4 for n > 16. A new aspect of these measurements is the use of a pulse amplified single frequency continuous wave laser to drive the transition from the bound 6snk states to the autoionizing 6pnk states. We have developed a reliable method for wavelength calibration based on absorption by I2 lines and transmission though a Fabry Perot etalon, and we have observed a spectral resolution of 300 MHz, substantially less than the Doppler width of the transition. In fields of less than 20 V/cm the Ba 6p1/2nk Stark states composed of l > 4 states span an energy less than the autoionization width of the Ba 6p1/2nh state, and the spectra exhibit unusual satellite structure, which we are able to reproduce in a simple model. The model is based on an incomplete Stark manifold and a three channel quantum defect theory.

Using Strong Optical Fields to Manipulate and Probe Coherent Molecular Dynamics

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Funding:	$145,000

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. Ultimately, through the application of these methods, we will work to obtain a more complete picture of the non-perturbative response of molecules to strong laser fields. Optical pulses and pulse sequences with well-defined optical phase (e.g., the relative phase between two optical fields, the time delay between the peak in the intensity envelope of a few-cycle optical pulse relative to the maximum field, or the absolute phase of an optical field relative to the center of the intensity envelope of a second pulse) are particularly useful for these studies. Such fields can assert and/or probe time-dependent, laboratory-fixed directionalities. This capability, particularly when used in combination with preferentially oriented molecular targets, can enable experiments in which electrons are driven in specific directions within molecules to probe and influence time-dependent molecular structure and dynamics.

New Scientific Opportunities Through Inelastic X-Ray Scattering at 3rd-and 4th-Generation Light Sources

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Funding:	$164,000

The goal of this program is to broaden the range of applications of resonant and nonresonant inelastic x-ray scattering and x-ray emission spectroscopies at both third and fourth generation light sources. This includes the long-term goal of enabling and performing studies of x-ray nonlinear and/or nonequilibrium effects at XFEL facilities. To this end we have been developing new variants of high-throughput x-ray emission spectrometers, and then using these instruments to investigate problems of interest to DOE. This includes work on transition-metal oxide battery electrodes, commercial catalysts, fuel-cell membrane materials, photosynthetic complexes, phosphor materials, and methods to enhance the detection thresholds for XAFS studies of trace levels of heavy metal contaminants. The phosphor studies fill an important further pedagogical role, by demonstrating the application of time-resolved high-resolution XES as a tool for understanding structural changes and energy transfer mechanisms in situations where optical spectroscopies are often inapplicable. Several of these studies also lay important groundwork for future ultra-fast x-ray studies of local atomic, electronic or magnetic structure, such as at the LCLS.

Advanced Instrumentation for Ultrafast Science at the LCLS

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Funding:	$1,500,000

This funding is for building a facility that will be housed at the LCLS and that can be used by any DOE-BES scientist. We have been designing and purchasing equipment for the construction of two instruments that will be operated by the LCLS. The instruments should be ready for use in September/Fall of 2012. These instruments will be available to all LCLS users from any scientific community, some of which are funded by DOE-BES.

The instruments are (1) An x-ray split and delay (XRSD) to allow x-ray pump/x-ray probe experiments and (2) an experimental system that encompasses several detectors and allows ion-ion coincidences and electron imaging. This second instrument is called LAMP to reflect the collaboration among LCLS, ASG (Max Planck Society), and WMU for the construction of the project. Each party contributes funds, equipment, postdoctoral students, scientists, and engineers. The PI funding would not have allowed the scope of the advanced instrumentation without the collaboration with LCLS and the Max-Planck Society.

Probing Complexity Using the ALS and the LCLS

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Funding:	$180,000

Our research program focuses on furthering the understanding of fundamental interactions between photons and complex systems and advances the knowledge of the properties of these systems. We intend to study the relaxation mechanisms that are important when inner-shell electrons in correlated systems interact with photons from two light sources: (1) an ultrafast, intense x-ray free electron laser (FEL), the Linac Coherent Light Source (LCLS) at the Stanford Linear Accelerator Center (SLAC), and (2) a long pulse weak-field synchrotron source, the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. Our research will be conducted in a strong partnership with theorists to make effective and significant advances. Our proposed experiments will be carried out using various advanced methods such as ion imaging, ion-ion and electron-ion coincidence techniques, angle-resolved photelectron spectroscopy, and photoion-spectrometry.

We propose detailed investigation of inner-shell excitation in selected atoms, molecules, clusters and their ions with photons at different wavelengths, intensity regimes and photon-pulse duration. These studies may lead to the control of fundamental properties of matter, and advance knowledge of non-linear physics and many-body dynamics. The latter is a problem of central importance to many fields related to physics since it is the correlated motion of electrons that is responsible for the structure and many properties of matter, including chemical reactions and superconductivity. These investigations will sample directly the quantum mechanical wave functions used in models which we seek to test or stimulate. The understanding of how electronic and nuclear motions are coupled by electronic excitation still presents serious experimental and theoretical challenges. Also, the proposed research may enable progress in other areas of science, with the better understanding of more complex systems such as bulk materials or biological specimens. For example, we will contribute to the understanding of radiation damage that occurs in single biomolecule imaging. We may also provide, through our cluster studies, understanding of intense laser-matter interaction, relevant to matter under extreme conditions. Thus, our AMO program will underpin other research programs important to the DOE, BES mission.

This program has trained many students who graduated with masters and PhD and who are now employed.

Structure From Fleeting Illumination of Faint Spinning Objects in Flight

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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. Progress in five areas is reported below.

(1) Computationally efficient 3D structure recovery from XFEL snapshots. Previous algorithms for single-particle structure recovery from random snapshots, including those developed by us, were based on computationally inefficient Bayesian inference. Using newly discovered symmetries underlying image formation by scattering, we have demonstrated a computationally efficient approach able to reconstruct objects with computational complexities 104x higher than previously possible.

(2) Efficient, unsupervised extraction of useful snapshots from large XFEL datasets. Ideally, XFEL experiments produce diffraction snapshots of an object (or a series of identical objects) viewed in different orientations, from which 3D structure can be retrieved. In practice, the datasets consist of unsorted admixtures of blank snapshots, and a variety of snapshots emanating from one or more particles belonging to a number of species. We have developed and demonstrated an unbiased, accurate, and computationally efficient method for classifying experimental X-ray diffraction snapshots without recourse to operator supervision, specific noise models, or templates.

(3) Structure recovery from ultra-low-dose image snapshots. Cryo-electron microscopy (Cryo-EM) currently sets the bar for 3D structure recovery from random snapshots in terms of spatial resolution (~0.3nm) and has begun to produce dynamic information by mapping biologically important reactions. Using the newly discovered symmetries of image formation, we have demonstrated 3D structure recovery from cryo-EM snapshots at 12x lower dose than currently possible.

(4) 3D movies of biological entities (in progress). There is mounting evidence that structural variability is common in biology and important to function, and that "structure" is neither static, nor immutable. We are developing a new generation of algorithms to structure and dynamics (3D movies) from random sightings of heterogeneous ensembles, such as collections of molecules each at a different part of a chemical or biological process. This would revolutionize our ability to understand the connection between structure and function in life and energy sciences.

(5) Structure recovery for complex objects such as whole cells. We have developed a conceptual framework for determining the structure of up to a million configurationally and compositionally heterogeneous cells with datasets expected from the Next Generation Light Source. This has formed a key part of the scientific case for the NGLS, of which one of us is a Principal Investigator.

(6) Ultrafast molecular processes beyond timing jitter. In conjunction with P. Bucksbaum et al., we have studied ultrafast, X-ray induced fragmentation of molecular nitrogen. The temporal resolution of time-resolved LCLS experiments is limited by timing jitter, measured to be ~ 300fs FWHM. Using advanced manifold-based analytical techniques, we have succeeded in revealing ultrafast processes much shorter than the timing jitter. These results have potentially broad implications for the study of ultrafast molecular processes.

Production and Trapping of Ultracold Polar Molecules

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The goal of our project is to produce and trap a gas of polar molecules at ultracold temperatures and substantial density. Once achieved, a variety of novel quantum effects associated with the low temperatures and/or the polar nature of the molecules (such as control over collisions and chemical reactions with electric fields) should be observable. We are building on previous results from our group, where we demonstrated the ability to assemble RbCs polar molecules from laser-cooled and trapped Rb and Cs atoms. This assembly method uses laser light as a sort of catalyst for the sticking together of atoms, in the process known as photoassociation. We previously showed that we could trap the molecules as they were formed in states of high vibrational excitation, and that (without trapping) we could transfer a small fraction of the excited molecules to their absolute lowest energy state.

In the current period, our goal has been to combine these methods and to improve the efficiency of transfer to the internal ground state. We have made progress on several fronts. For example, we have obtained detailed spectroscopic data on the energy levels of the RbCs molecule that are involved in the state transfer process; these details must be understood to devise an efficient transfer scheme. We are presently working with theorists to interpret this data. In addition, very recently we discovered a method to produce absolute ground-state molecules in a single step, without the need for an additional transfer stage. Although the efficiency of this direct photoassociation process is low, its intrinsically dissipative nature allows the continuous accumulation of ground-state molecules for long intervals. We estimate that already this simpler method could result in a similar overall number of trapped ground-state molecules as would be available from the multi-step process, and are investigating potential further improvements.

In addition, we have pursued several related projects. For example, we investigated theoretically how energy levels of polar molecules are modified when trapped by laser light, in the presence of a polarizing electric field. This study has broad implications for experiments that plan to use polar molecules for quantum simulation of many-body systems and/or quantum information processing. We have also begun developing a new experimental diagnostic technique to enable imaging of very tenuous clouds of molecules. This method uses photoionization and time-of-flight mass spectroscopy to detect specific molecular species and energy states, plus a novel system of ion optics to enable high magnification-imaging of the original ions’ positions.

DOE National Laboratories

Atomic, Molecular and Optical Physics

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Funding: $1,825,000

The Argonne AMO physics program seeks a quantitative understanding of x-ray interactions with atoms and molecules from the weak-field limit explored at the Advanced Photon Source (APS) to the strong-field regime accessible at the Linac Coherent Light Source (LCLS). This is a combined experimental and theoretical effort.

The Argonne AMO group has led three experiments at the LCLS to establish the fundamental interactions of high-intensity x-rays with matter and to explore potential applications of ultraintense x-ray radiation. In 2010, initial experiments at LCLS established that, for non-resonant interactions, sequential single-photon absorption with high-fluence, high-intensity x-ray pulses dominate the interaction. Hollow-atom formation is prevalent and creates a transient x-ray transparency. This year, the effect of transient hollow-atom formation on x-ray elastic scattering was evaluated theoretically, and found to alter the scattering pattern for carbon at fluences of 10^6 – 10^8 x-rays/Å^2 which in turn deteriorates resolution beyond ~1.7 Å. Going beyond non-resonant x-ray interactions, the analysis of Rabi flopping of an inner-shell electron by driving the 1s-2p transition in a neon ion was completed and a paper accepted for publication. The Rabi-flopping signature was broadening of the resonant Auger line, and the effect, though small, was clear and was predicted to be more readily visible with temporally coherent, Gaussian pulses, as opposed to the chaotic SASE pulses currently available at the LCLS. Importantly, the method used to reveal the 1s-2p transition (i.e., using the first portion of a high-fluence pulse to produce the desired target can unveil resonances with cross sections >1000x larger than in the original target, and thus can potentially unleash damaging Auger cascades).

The group also played a major role in the analysis and publication of a study of direct two-photon absorption, a traditional nonlinear process, in helium-like neon. Competition with sequential two-photon absorption, due to a previously ignored nearby resonance, is hypothesized to be responsible for the discrepancy between the observed and previously calculated direct two-photon absorption cross-section. In addition, the group contributed to efforts to characterize the SASE LCLS pulses using two-color laser/x-ray pump-probe methods, leading to the first publication using this technique at LCLS. This work confirmed our earlier deduction that the x-ray pulses were substantially shorter than the electron pulses. Previously, we suggested x-ray two-photon photoelectron spectroscopy could be developed into an important diagnostic tool with greater chemical sensitivity than standard x-ray photoelectron spectroscopy. An experiment at LCLS was conducted on a molecule containing carbon, nitrogen and oxygen to explore this possibility. Toward this goal, analysis of the double-core-hole electron spectrum in formamide is underway.

Theoretically, a novel scheme to extend the photon energy range of high-order harmonic generation (HHG) was proposed. The basic idea is that simultaneous irradiation of an atom with intense optical and x-ray radiation will upshift HHG radiation by the binding energy of a core electron – as during the recombination process, a core hole is present. A two-electron quantum theory for this situation was developed and published. A scheme to optically control x-ray lasing was also investigated.

Ultrafast X-ray Imaging of Laser-Controlled Molecular Motions

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Funding:	$847,000

Ultrafast x-ray imaging of laser-controlled molecular motions unites a Grand Challenge theme of photonic control of matter with the most advanced photon probes available – ultrafast tunable, polarized x-rays. Previously the principal investigators and their collaborators developed an x-ray microprobe of laser-aligned molecules. This was the first time that the efficient combination of x-ray and laser alignment techniques had been experimentally demonstrated. A central goal here is to extend the x-ray microprobe methodology to x-ray diffraction imaging of laser-aligned molecules. This is an important step toward x-ray imaging of molecules that cannot be crystallized. Here we investigate x-ray probes of systems ranging from laser-aligned small molecules in the gas phase to laser-aligned nanoobjects or laser-excited molecules in solution. This is possible only with x-rays as an in situ probe of matter in the focus of an intense laser field. At present, x-ray pulses available at Argonne's Advanced Photon Source are ~100 ps in duration, sufficient to image molecules aligned in the presence of laser fields. In the near future, the Short Pulse X-ray Facility (SPX) promises tunable, polarized, ultrastable pulses of ~1-100-ps duration at the full repetition rate of the Advanced Photon Source. SPX will enable x-ray imaging with joint picosecond and picometer resolution. The SPX facility was guided through the many steps of the review process this year.

During this past year, high-repetition-rate laser pump/x-ray probe methodologies using x-ray microprobe techniques have been realized at the Advanced Photon Source. An in-depth article describing the experimental scheme has been published. Development of this high-repetition-rate methodology allows the entire flux of the APS to be used for time-resolved studies, providing a statistical gain of ~6000 over standard 1 kHz lasers. Combined with microprobe techniques, the per-pulse fluence at even the highest repetition rate, 6.5 MHz, can saturate typical molecular transitions. With this apparatus, we performed the first-ever simultaneous measurement of x-ray absorption, x-ray emission and x-ray diffuse scattering on a laser-excited molecule, the spin-crossover complex iron(II)-tris(bipyridine), in collaboration with a large, multinational European group. The analysis is underway, aiming toward the dream of precision monitors of both inner-and outer-sphere response to optical perturbations.

During this past year, progress on x-ray imaging of single trapped and aligned nanoparticles in solution proceeded on two fronts: (1) x-ray imaging of single metal nanoparticles on a solid support and (2) the development of optical trapping and manipulation techniques for metal nanoparticles. X-ray diffraction imaging of immobilized silver and gold nanowires was performed in a Bragg coherent diffraction imaging CDI geometry. The Bragg CDI geometry will be immediately transferrable to imaging of trapped nanoparticles in solution. We have also completed design and begun construction of a compact, portable optical trapping apparatus that can be used at the APS beamlines. Assembly and testing of this apparatus is being performed in a recently completed laser laboratory at Argonne's Center for Nanoscale Materials. In parallel, optical trapping techniques appropriate for metal nanoparticles are being developed at the University of Chicago.

Atomic, Molecular and Optical Sciences at LBNL

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Students: 3 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $1,485,000

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) a 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.

Ultrafast X-Ray Science Laboratory (UXSL)

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Students: 5 Postdoctoral Fellow(s), 4 Graduate(s), 0 Undergraduate(s)
Funding: $2,120,000

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 Ultrafast X-ray Science Laboratory are an integrated effort to develop novel applications of emerging ultrafast experimental techniques and to provide basic knowledge that is central to the programmatic goals of BES/DOE.

Engineered Electronic and Magnetic Interactions in Nanocrystals

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Funding: $800,000

Using nanocrystal quantum dots one can produce extremely strong spatial confinement of electronic excitations 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. In addition to spectral tunability, 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 induced by electron-hole exchange coupling, ultrafast mutiexciton decay via Auger recombination, and direct generation of multiple excitons by single photons via carrier multiplication. Confinement-induced mixing between the conduction and the valence band can also lead to interesting peculiarities in magnetic interactions such as switching of the sign of the g-factor in magnetically doped nanocrystals. The major thrust of this project is to understand the physics of electronic and magnetic interactions under conditions of extreme quantum confinement, and to develop methods for controlling these interactions. Research topics explored here include (1) control of Auger recombination via engineered exciton-exciton interactions in heterostructured and alloyed nanocrystals with a goal of realizing the regime of continuous-wave lasing, (2) new functional behaviors via nanocrystal doping with optically active ions such as copper, (3) control of single-exciton dynamics via tunable fine-structure excitonic splitting, and (4) controlled exchanged interactions in magnetically doped NCs probed by steady state and time-resolved magneto-optical spectroscopies.

Understanding and Controlling Atomic Scale Matter

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

The overarching theme is development of a fundamental understanding of the interactions of atomic scale systems, such as photon-atom, ion-atom, ion-ion, or ion-solid collisions, and the 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 the Holifield Radioactive Ion Beam Facility and 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 heavy ion storage rings. Higher energy electron-molecular ion interactions are also studied at MIRF employing crossed-beams capabilities. Experiments are complemented and extended through theoretical and computational studies. 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.

PULSE: The Stanford Photon Ultrafast Laser Science and Engineering Center

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Students:	10 Postdoctoral Fellow(s), 8 Graduate(s), 0 Undergraduate(s)
Funding:	$3,152,000

Tasks supported by the Chemical Sciences FWP are aimed at the control and imaging of chemical dynamics, from electrons in small molecules to atoms in clusters. The emphasis is on Grand Challenges for energy science. The proposed research utilizes our core strengths in molecular theory (Martinez), ultrafast spectroscopy (Gaffney), quantum control (Bucksbaum), ultrafast x-ray-matter interactions (Reis), and strong field AMO physics (Gühr and Bucksbaum). The imaging expertise in PULSE includes biological imaging (Bogan) with laser manipulation of targets for imaging (Bucksbaum) and our special abilities to capture and image ultrafast processes as they happen. Tasks in this area utilize the PULSE Institute building as well as SPEAR3 and the LCLS AMO, SXR, CXI, and XPP end stations. Subtasks include the following.

Attosecond Coherent Electron Dynamics (ATO) [Task Leaders Markus Gühr, Todd Martinez, and P. Bucksbaum]: This task studies the fastest timescales in chemical physics involved with electron correlation, and nonradiative chemical processes, connecting LCLS research to the new field of attophysics.

Strong Fields in Molecules (SFA) [Task Leader Phil Bucksbaum and David Reis]: This task incorporates and extends strong-field quantum control to LCLS experiments in molecular dynamics and molecular imaging. Strong field effects in atoms and molecules can be studied using ultrafast x rays, or employed to create targets for x-ray imaging. In addition, LCLS is itself the world’s first source of coherent volt/Ångstrom fields of x-ray radiation. A separate component of this program in ultrafast x-ray scattering is in the Nonequilibrium Dynamics in Solids task.

Solution-Phase Chemical Dynamics (SPC) [Task Leader Kelly Gaffney]: This task explores ultrafast chemical processes in solutions, utilizing LCLS, synchrotrons, and the PULSE labs. Emphasis is on the ultrafast dynamics of energy conversion in chemistry.

Nonperiodic Imaging (NPI) [Task Leader Michael Bogan]: This task studies nonperiodic nanoscale imaging, one of the greatest new opportunities for LCLS. The frontier science questions under study range from nanobiology to aerosol chemistry to combustion.

Find out more: http://pulse.slac.stanford.edu.

Catalysis Science

Institutions Receiving Grants

High Temperature Chemistry of Aromatic Hydrocarbons

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Funding:	$165,000

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. The work falls broadly into three categories: (1) the continued search for new high-temperature reactions that have no counterpart under ordinary laboratory conditions, (2) the execution of experiments devised to establish mechanistic details of these distinctive high temperature reactions, and (3) the design, preparation, and examination of PAHs that are predicted to provide additional examples of recently discovered high-temperature reactions.

Ancillary to these primary objectives, numerous investigations into the properties of unusual products obtained as a result of high temperature transformations have been made possible by this research, often through collaborations with experts in other fields.

The efficient production of clean energy from fossil fuels will remain a major component of the DOE mission until alternative sources of energy eventually displace coal and petroleum. Hydrocarbons constitute the most basic class of compounds in all of organic chemistry, and as the dominant species in fossil fuels, they figure prominently into the programs of DOE. 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, including more complex processes 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.

Considerable progress has been made on this project in several areas. From carbon-13-labeling studies, it has been found that carbon atoms in adjacent positions in PAHs swap places with one another at high temperatures. The process appears to be universal and has been demonstrated to occur even in benzene. The ease of 1,2-switching correlates with the double bond character between the two positions in the PAH, and the mechanism is now understood to involve reversible thermal ring contractions of benzene rings. Aromatic hydrocarbons that contain bay regions undergo unique thermal transformations resulting in the loss of two hydrogen atoms, irreversible destruction of one benzene ring, and rearrangement of the carbon skeleton to one that maps onto fullerenes, with two new five-membered rings. Mechanistic studies reveal that this process involves thermal cyclodehydrogenation in the bay region, followed by a pair of hydrogen-shift/ring-expansion rearrangements. Numerous gas phase rearrangements of aryl radicals have been predicted and revealed experimentally, including 1,2-shifts of hydrogen atoms and aryl groups, 1,3-shifts of hydrogen atoms, phenyl groups, and ethynyl groups, 1,4-shifts of hydrogen atoms, and 1,5-shifts of hydrogen atoms. The proposed buildup of larger PAHs from smaller ones (e.g., in the processes leading to soot formation) through the capture of acetylene by an aryl radical has been verified experimentally. The mechanisms governing thermal cyclodehydrogenations that form five- and six-membered rings and the thermal cleavage of aryl-aryl bonds have also been investigated.

Advances in chemistry at the most fundamental level come about primarily from the discovery of new reactions and from new insights into how reactions occur. Harnessing that knowledge is the key to new technologies. The recent commercialization of a combustion synthesis of C60 and other fullerenes depended critically on the knowledge of hydrocarbon reactions at high temperatures in the gas phase; the research supported by this project can be expected to enable further advances in the realm of carbon-rich materials.

Catalysis, Dynamics and Stability of Enzymes Under Extreme Conditions

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Funding:	$170,000

After our surprise finding that the cofactor Mg^{2+}, traditionally described to be essential for phosphoryl transfer reactions, also dramatically accelerates the lid opening of the enzyme (the rate-limiting step for adenylate kinases), we made big strides in characterizing the energetic contributions of Mg^{2+} to the free energy landscape of the enzymatic cycle.

First, we performed pre-steady state kinetics using quenched-flow methods coupled with HPLC to measure the role of Mg^{2+} on the kinetics of the phosphoryl transfer step and the lid-opening step. Using a number of different divalent cations in this assay we started to figure out the molecular basis of catalysis performed by Mg^{2+} for these two independent steps. The P-transfer is highly specific for Mg^{2+} because it seems to be optimized for the right charge/ionic radius ratio. In contrast, other divalent cations can well catalyze the lid-opening step.

We finally were able to obtain an x-ray structure of natural substrates (two ADP) bound to the active site together with a divalent cation, Co^{2+}. Recently, we solved the structure of the enzyme with the transition state analogue Mg/AlF_4 (bound right between ADP and AMP). Finally, we measured the role of Mg^{2+} for protein dynamics using NMR relaxation dispersion and MD simulations.

These results suggest new mechanistic insight into kinase function, or even more widely for phosphoryl transfer reactions, and are summarized as follows:

(1) Mg^{2+} helps anchor the flexible donor phosphoryl group positioning it for more favorable attack by the attacking oxygen atom of the acceptor nucleotide, suggesting a significant entropic benefit to catalysis by the cofactor.

(2) Water molecules liganded to the metal ion are remarkably stable and remain coordinated during the lifetime of the simulation, thereby hampering the unwanted hydrolysis reaction.

(3) Mg^{2+} may activate the leaving group and or nucleophile for the P-transfer.

(4) Mg^{2+} vastly accelerates a conformational change subsequent to P-transfer, with the mist likely due to a direct charge contribution.

(5) One atom, Mg^{2+}, accelerates two subsequent steps in the enzymatic cycle.

(6) An active site Arg contributes another three orders of magnitude to catalysis of P-transfer.

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

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Funding:	$150,000

Recent attention in the chemical community has been focused on the energy efficient and environmentally benign conversion of abundant small molecules (CO_2, H_2O, etc.) to useful liquid fuels. This project addresses these goals by examining fundamental aspects of catalyst design to ultimately access small molecule activation processes under mild conditions. Specifically, heterobimetallic complexes that feature a hard, Lewis acidic early transition metal center and a soft, Lewis basic late metal center are being targeted. Unlike bimetallic complexes featuring identical or similar metals, the bonds between metals in early/late heterobimetallics are dative in nature, with the electron-rich late metal center donating electron density to the empty d orbital(s) on the electron-deficient early metal center. The polar character of these metal-metal bonds suggests that heterolytic cleavage of bonds in small molecule substrates across metal-metal bonds of this type is a promising reaction pathway. In addition, dative interactions between metal centers should have a dramatic effect on the redox activity of both transition metals, providing a mechanism to tune redox potentials and access substrate reduction/activation at mild overpotentials.

The initial objective of the project is to synthesize early/late heterobimetallic complexes linked by bifunctional phosphino(amide) ligands, varying both the bridging ligands and the transition metals. Crystallographic (X-ray) and theoretical (DFT) methods will be used to examine the nature of the polar MM interactions and determine the factors that strengthen or weaken these interactions. To assess the effect that metal-metal interactions in early/late heterobimetallics have on their redox behavior as compared to monometallic species, cyclic voltammetry will be used. Preliminary data have already shown that dative metal-metal interactions in CoZr species increase the two-electron reduction potential of Co by nearly ~1 V. Once these heterobimetallic complexes have been fully characterized, the ability of these complexes to activate and functionalize small molecule substrates such as CO_2, O_2, H_2, and N2 will be examined under both stoichiometric and catalytic conditions.

This research project will provide a better fundamental understanding of how interactions between early and late transition metals can be used as a strategy to promote and/or control chemical transformations related to the clean production of fuels.

Structural and Kinetic Studies of Novel Cytochrome P450 Small-Alkane Hydroxylases

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Funding:	$80,000

We are investigating the structures, biophysical properties, and kinetics of members of two families of cytochrome P450s that have been evolved in the laboratory to catalyze the hydroxylation of gaseous alkanes. Activity towards propane, ethane, and methane have not been previously reported for any naturally-occuring cytochrome P450, yet we have shown that highly proficient small-alkane P450 hydroxylases are possible and, indeed, easily accessible by mutation from existing P450s. One laboratory-evolved enzyme, derived from the fatty acid hydroxylase P450 BM3 (CYP102A1 from Bacillus megaterium), inserts oxygen primarily at the 2-position of propane. We also found a member of the newly-characterized longer-chain alkane hydroxylase CYP153 family, CYP153A6 to hydroxylate propane and butane and do so primarily at the energetically disfavored terminal carbon (1-position). These heme enzymes are unrelated mechanistically and evolutionarily to the monooxygenases that are known to hydroxylate C1-C4 alkanes in alkanotrophic organisms and therefore offer a new mechanism and catalytic platform for selective oxidation of small alkanes.

With a collection of small alkanes hydroxylating cytochrome P450s, we are able to investigate differences between the active oxidants generated within the enzymes that are responsible for catalysis. By studying the reactivity of enzyme oxidants generated chemically, we can determine the substrate range of the active catalyst independent of the substrate recognition limitations of the enzyme fold. This basic understanding will aid further evolution or design of a possible methane-hydroxylating cytochrome P450 and P450 catalysts for selective alkane oxidation. It will also provide inspiration for future design of new biomimetic catalysts for these key conversions, including the conversion of methane to methanol. We have also obtained the x-ray crystal structure of a key evolutionary intermediate along the pathway to the propane-hydroxylating P450 BM3. This structure helps to explain the broad substrate specificity of this intermediate, which allows it to be optimized by directed evolution for activity on substrates that range from propane to large pharmaceutical molecules.

Synthetic and Mechanistic Investigation of Polymerization Catalyzed for Early Transition Metal Compounds

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Funding:	$185,000

Catalytic science will continue to make major contributions to some of the foremost concerns of modern chemical research: the development of new processes for producing commodity chemicals that are more energy-efficient and less wasteful and polluting. Polymerizations of ethylene, propylene, and styrene are very important catalytic processes that have grown to a worldwide production that now exceeds tens of billions of pounds per year. New "single site" catalysts continue to be developed by the polyolefin industry, particularly for ethylene/1 alkene copolymers as well as ethylene/propylene and ethylene/propylene/diene elastomers. Our studies are fundamental to an understanding how these catalysts function and are intended to provide guidance for the development of new catalysts for producing even more useful materials based on polyolefins.

Controlling Selectivity of Heterogeneous Catalysts Using Grafted Metallocalixarene Active Sites

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Funding:	$150,000

Isolated active sites for catalysis enable bioinspired functional material design using a toolkit approach, which is based on active sites consisting of preferentially arranged chemical groups – having precise atomic composition and connectivity. This project addresses the synthesis of such isolated active sites, which place metal cations and molecular complexes onto surfaces within preferred environments, and lead to refined degrees of control of heterogeneous catalysis. These tools are specifically applied for control of hydride and oxygen transfer Lewis acid catalysis. The project builds on emerging synthetic methods in the synthesis of surface complexes based on grafted calixarene scaffolds using various cations, and applies these tools toward the understanding of the role of coordinative unsaturation at the active site in these catalyzed reactions, as well as controlling chemoselectivity and, in particular, enantioselectivity, of catalysis.

Research activities specifically build on a rapidly emerging basis of knowledge relating to use of metallocalixarene complexes as active olefin epoxidation and ketone reduction catalysts (Meerwin-Pondorf-Verley – MPV – reaction). Recent research activity in the Katz group has demonstrated the use of novel Al(III)-calixarene complexes as catalysts for the former, and has focused on fundamental properties of catalyst and reactant that control catalysis. These studies have elucidated two-point reactant binding as a crucial factor to achieving an order of magnitude higher reaction rates. These catalysts have recently been successfully heterogenized in two coordination spheres. One of these consists of an open coordination site on the grafted Al(III)-calixarene center, whereas the other is closed and has no such open coordination site. Our recent results are the first to demonstrate that MPV catalysis is inactive using the latter-type site, whereas it is highly active using the former-type site. These are the first results to control and elucidate requirements for open and closed coordination sphere in a heterogeneous catalyst active site. We have furthermore recently demonstrated that, unlike MPV catalysis, epoxidation catalysis proceeds in an active fashion with the closed Al(III)-calixarene centers. This observation strongly suggests direct coordination of hydroperoxide oxidant during epoxidation catalysis. In addition, proposed research leverages on recent advances in the Katz group relating to synthesis of the most highly enantioselective MPV catalysts to be reported to-date, which exhibit ee's above 99% for certain reactions.

The fundamental investigations underway as part of this project are expected to broadly impact a variety of areas relevant to heterogeneous catalysis and adsorption. A key general aspect that will be investigated permits placing chiral functional groups in close proximity to the Lewis acidic metal center and enabling the synthesis of highly enantioselective heterogeneous catalysts. Another key aspect revolves around understanding the preferential electronic environment and extent of electron delocalization at the Lewis acid active site. Yet another key aspect undertaken in the project is in understanding the role of coordinative unsaturation at the metal center for both hydride and oxygen transfer reactions. These aspects are geared to expand the synthetic toolkit of possibilities for heterogeneous catalyst design in the future, and include photooxidation applications as well as the possibility of applications in solar energy conversion.

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

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Students:	1 Postdoctoral Fellow(s), 4 Graduate(s), 1 Undergraduate(s)
Funding:	$300,000

By use of the precursor $Ir(CO)_2(acac)$ [acac is acetylacetonate], a ship-in-a-bottle synthesis was used to prepared $Ir_6(CO)_{16}$ and, by decarbonylation, clusters well approximated as Ir_6 in the supercages of zeolite NaY. The samples were characterized by IR and EXAFS spectroscopies and imaged by aberration-corrected scanning transmission electron microscopy (STEM) with a high-dose electron beam (~10^8 e^-/$Å^2$, 200 kV), and the catalyst performance was characterized by turnover frequencies for ethene hydrogenation at 298 K and atmospheric pressure. The images characterizing a sample with about 17% of the supercages occupied by decarbonylated nanoclusters indicated clusters well approximated as Ir_6, with diameters consistent with the presence of Ir_6 clusters, and some of the images showed the clusters with atomic resolution and indicating each of the 6 Ir atoms. The cluster size was confirmed by EXAFS spectra. Two bonding positions of the Ir_6 clusters in the supercages were distinguished; 25% of the clusters were present at T5 sites and 75% at T6 sites. The results represent the first example of the application of high-dose electron beam conditions to image metal nanoclusters in a porous material; the data are characterized by a high signal-to-noise ratio, and their interpretation does not require any image processing or simulations. These statements are based on images determined in the first 5 s of exposure of the catalyst to the electron beam; thereafter, the electron beam caused measurable deterioration of the zeolite framework and thereupon aggregation of the iridium clusters.

$Ir(C_2H_4)_2(acac)$ was used as a precursor to form $Ir(C_2H_4)_2$ complexes bonded by two oxygen atoms to the interior surface of the zeolite SSZ-53. Using aberration-corrected STEM, we imaged iridium atoms in the site-isolated iridium complexes in the one-dimensional non-intersecting 14-ring channels of this zeolite. STEM allowed tracking of the movement of the iridium atoms in the channels, and the images demonstrate the interaction of iridium with the zeolite framework (channel confinement), and they also providing a direct visualization of the initial steps of metal nanoclusters formation, which occurred under the influence of the electron beam and also when the sample was treated in hydrogen. The key to successful imaging of the supported mononuclear iridium complexes was quick, deft imaging of the sample with high-dose beam conditions; images were collected within 5 s. With continued recording of images, there was clear evidence of destruction of the zeolite framework structure, which allowed the formation of iridium clusters as a results of the removal of the channel confinement. The results demonstrate how STEM can be used to help design improved catalysts by identifying the catalytic sites and observing how they change in reactive atmospheres.

Leveraging recent breakthroughs in the synthesis and characterization via single-crystal X-ray diffraction of calixarene phosphinite, phosphite, and carbene Ir_4 carbonyl clusters, we are combining computation and experiment with the goal of understanding fundamental electronic effects that govern when carbonyl ligands adopt bridging vs. terminal configurations in monosubstituted calixarene Ir_4 carbonyl clusters. Moreover, the mechanism of decarbonylation within the clusters is being modeled with a combined computational-experimental approach. Experiments suggest that this mechanism is based on a conversion of bridging carbonyls to a terminal carbonyls, followed by release of terminal CO. We are starting synthetic efforts that will place calixarene-bound Ir_4 clusters onto two-dimensional zeolitic supports, such as the recently discovered UCB-1. The experiments wherein the local environment surrounding the Ir_4 is well ordered both from the top (calixarene) as well as below (two-dimensional zeolite) are aimed at paving the way to EXAFS characterization of of calixarene-bound catalysts in action during ethylene hydrogenation. Solid-state NMR experiments with PNNL collaborators are being planned to kinetically investigate reactive treatments of anchored Ir_4 calixarene phosphine complexes and to correlate measured kinetics with in-situ IR spectroscopy.

Tailoring Supports as Ligands: Zeolites and Oxides as Hosts of Molecular Metal-Complex Catalysts

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Funding:	$200,000

Zeolite- and MgO-supported mononuclear iridium diethene complexes and rhodium diethene complexes were formed by the reaction of $M(C_2H_4)2(acac)$ (acac = acetylacetonate, $C_5H_7O_2$–; M = Ir or Rh) with each support. Changes of the ligand environment of the supported metal complexes were characterized by IR, XANES, and EXAFS spectroscopies as various mixtures of H_2, C_2H_4, and CO flowed over the samples. In contrast to the nonuniform metal complexes anchored to metal oxides, our zeolite-supported metal complexes were highly uniform, allowing precise determinations of the chemistry, including the role of the support as a macroligand. Zeolite- and MgO-supported $M(C_2H_4)2$ complexes are each rapidly converted to M(CO)2 upon contact with a pulse of CO, and the CO stretching frequencies indicate that the metal is more electron-deficient when the support is the zeolite. The Ir(CO)2 complex supported on MgO was highly stable in the presence of various combinations of CO, C_2H_4, and helium. In contrast, the zeolite-supported Ir(CO)2 complex was found to be highly reactive, forming Ir(CO)3, Ir(CO)(C_2H_4), Ir(CO)2(C_2H_4), and Ir(CO)(C_2H_4)2. The pi-bonded ethene ligands of the zeolite-supported Ir(C_2H_4)2 in H_2 were facilely converted to sigma-bonded ethyl. However, the stability of the ethene ligands was markedly increased when the support was changed to MgO or when a CO ligand was simultaneously bonded to the iridium. The rates of catalytic ethene hydrogenation and H_2/D_2 exchange in the presence of a catalyst initially consisting of Ir(C_2H_4)2 on the zeolite were found to be more than an order of magnitude higher than when MgO was the support. The iridium complexes containing one or more CO ligands were found to be inactive for H_2/D_2 exchange reactions when the support was MgO, but they were moderately active when it was the zeolite. The effects of the MgO and zeolite supports on reactivity and catalytic activity are attributed to their differences as ligands donating or withdrawing electrons, respectively.

The catalytic properties of a supported metal depend both on the structure of the metal species and these metal–support (metal–ligand) interactions. We resolved these effects in experiments with isostructural mononuclear iridium complexes and small iridium clusters on the two aforementioned supports that have contrasting electron-donor/acceptor properties. Spectra of the catalytic species during ethene hydrogenation show that the reaction rate is largely determined by the reactivity of the metal for H_2 activation. The catalytic activity of isolated Ir sites on MgO is markedly less than that of sites comprising several Ir atoms, as the neighboring sites perform complementary functions. However, the importance of the metal nuclearity is much less when the support is the zeolite, because then the interaction of reactants with iridium is determined by the support, a ligand that enables isolated Ir atoms to bond facilely to both hydrocarbon and hydrogen as catalytic reaction intermediates.

When the metal was rhodium instead of iridium in the supported diethene complexes, a striking support effect on the catalysis of ethene conversion in the presence of hydrogen was observed: the MgO-supported complex is 100% selective for hydrogenation, whereas the HY-zeolite-supported complex is selective for ethene dimerization. The results imply a new mechanism for C-C bond formation, involving an interplay between the supported rhodium complexes and neighboring proton-donor groups of the zeolite.

Advancing Chemistry with F Elements

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The objective of this research is to use the unique chemistry available from complexes of the lanthanides and actinides, as well as the closely related yttrium, to advance chemistry in energy-related areas. These metals 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.

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

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One of the most important challenges in transition-metal catalysis is determining the true nature of the catalytically active components. A common question regards the phase of the active catalysts: homogeneous, heterogeneous, or both. The answer to this question is difficult to discern by existing experimental methods because the simple presence of solid particles or soluble components does not imply catalytic activity. Especially difficult is determining if the catalysis is proceeding exclusively by one phase of catalyst.

We are addressing this challenge through developing a high-sensitivity and high-resolution single-particle fluorescence microscopy technique that differentiates between homogeneous and heterogeneous catalysis by imaging the location of reactivity. We devised an imaging method for polymerization of dicyclopentadiene with Grubbs' 2nd Generation Catalyst that determined the location of the early stages of the polymerization reaction. These experiments are the first imaging of transition-metal catalyzed polymerization using single-molecule/-particle fluorescence microscopy. By imaging single polymers and single crystals of catalyst, polymerization catalysis was revealed to be exclusively homogeneous rather than heterogeneous or both, information which would not be readily available through prior analytical techniques. Under conditions with both solid- and solution-phase ruthenium metathesis catalysts, such as in self-healing materials, these data suggest that the reactivity is solely from soluble molecular catalysts. We anticipate that this approach will have broad applicability to other systems, investigations of which are underway.

Design and Characterization of Novel Photocatalysts With Core-Shell Nanostructures

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Funding: $380,000

The overall goal of this project is to develop new photocatalysts for employing 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.

The specific objective for the second year of the project has been to establish the synthetic parameters for full control of the synthesis of our original yolk@shell architecture and to develop the tools to characterize those catalysts. In terms of the synthesis, we aimed at controlling independently 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 (DRIFT) 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 to measure simple catalytic oxidation reactions. Time-resolved measurements have also been implemented to follow the electronic transitions involved in the photon excitation, electron transfer, and electron-hole pair recombination processes.

We have made advances in all the specific objectives listed above. In terms of synthesis, extensive work has been carried out to establish the procedures for the preparation of yolk@shell structures with full independent control of metal particle sizes and shell sizes and thicknesses. Regarding spectroscopic measurements, our first measurements have involved using time-resolved luminescence to detect new electronic states introduced by the addition of gold to the titania shells. Lastly, DRIFT has been used to measure the uptake of CO on Au@TiO_2 nanostructures and the rates of reaction for the oxidation of CO with O_2.

Transition-Metal-Catalyzed hydroamination of Non-Activated Carbon-Carbon Multiple Bonds with Ammonia

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Funding:	$155,000

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 and hydrazine.

We have found that gold(I) complexes, bearing cyclic (alkyl)(amino)carbenes (CAACs) as ancillary ligands, promote the hydrazine hydroamination of terminal and internal alkynes, as well as of diversely substituted allenes. Moreover, using a variety of diynes as substrates, 1-aminopyrroles, 1H- and 4H-pyrazoles, and 4,5,6,7-tetrahydro-1H-indazoles were prepared in one step and in good to excellent yields. Therefore these hydroamination reactions using hydrazine constitute ideal initial steps for the preparation of heterocyclic bulk chemicals. Note that, despite the economical interest of using hydrazine, a chemical that is produced in bulk quantities, only one example of a transition-metal catalyzed functionalization of $H_2NN H_2$ had been reported before our work. The use of this reagent is hampered by several difficulties. Like ammonia, hydrazine easily forms Werner complexes, which are usually inert. $H_2NN H_2$ is known as a strong reducing reagent, which can induce the formation of inactive metal(0) particles, and hydrogenate substrates leading to saturated molecules. Our success is due to the use of the CAAC ligands, which make the corresponding gold-Werner complex reactive.

We have found a practical and versatile synthetic route allowing for the functionalization of the N-heterocyclic carbene (NHC) backbone, especially the 4- and 5-positions. When combined with the recent discovery of modular syntheses of N,N'-unsymmetrically substituted imidazolium salts, these results pave the way for the preparation of NHCs with virtually any substitution pattern, and therefore very different s-donating and p-accepting properties, which should have an important impact in catalysis.

Amines and boranes are the archetypical Lewis bases and acids, respectively. The former can readily undergo one-electron oxidation to give radical cations, whereas the latter are easily reduced to afford radical anions. We have prepared a neutral tricoordinate boron derivative, which acts as a Lewis base, and undergoes one-electron oxidation into the corresponding radical cation. This compound is isoelectronic with amines and phosphines, and is the first group 13 derivative that can behave as a L ligand opening a new chapter in coordination chemistry. Because of the lower electronegativity of boron, compared to those of nitrogen and phosphorus, these group 13 compounds are potential strong electron-donor ligands for transition metals, and therefore well adapted for reactions involving ammonia and hydrazine.

Hierarchical Design of Supported Organometallic Catalysis for Hydrocarbon Transformations: Structures and Dynamics of Active Sites

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Funding:	$540,000

This project aims to improve heterogeneous catalysts for hydrocarbon transformations such as olefin metathesis and cyclopropanation, giving them higher activities and stabilities and improved functional-group tolerance through rational design. The major challenges are to (1) understand the origins of support-induced activity in dispersed metal oxides, (2) understand catalyst deactivation at the molecular level, and (3) modify active site structures to promote activation, improve functional-group tolerance, and slow deactivation. The overall goals of this project are to develop a fundamental understanding of active site formation, structure and reactivity, and to use this information to design materials better suited to a wide range of applications. A second overall goal of this project is to enable the design of more robust, low-PGM oxidation catalysts, combining the materials chemistry of crystalline mixed metal oxides with detailed reactivity studies linking structure and function.

SPECIFIC OBJECTIVES FOR THE PERIOD 5/1/10-5/1/11

(1) Computational analysis of CH_3ReO_3 reactions. We directly compared experimental and calculated rates of reaction, to probe the robustness of our theoretical framework for predicting active site reactivity in CH_3ReO_3-based metathesis catalysts.

(2) Probing the origin of support acidity and its influence on active site formation. Experimentally, we explored the mutual influences of Lewis acidity and Brønsted acidity through site-selective adsorption of

molecular precursors, analyzed by spectroscopic and temperature-programmed methods. Computationally, we laid the ground work for a new model of acidity in amorphous oxide supports.

(3) Probing the spatial distributions of active sites on oxide surfaces. We explored the ability of self-terminating surface reactions (grafting) to isolate adsorbed molecules on highly dehydroxylated silica.

(4) Reactivity of crystalline mixed metal oxides. We explored the NOx storage capacity and NOx storage-reduction activity of Pd-substituted $BaCeO_3$, as well as its sulfur tolerance.

POTENTIAL IMPACT IN SCIENCE AND IN TECHNOLOGIES OF INTEREST TO DOE

A more efficient use of uncommon metals in large-scale or widely-distributed catalysts will extend the availability of these metals for new applications. A designed dispersion through association of molecular precursors with specific surface functional groups generates more active catalysts. The use of crystalline metal oxides as hosts has the potential to stabilize cationic forms of the metal ions and thereby preventing loss of activity through sintering.

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

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Funding:	$160,000

To create and characterize the activity of new catalysts predicted by density functional theory capable of activating C-x bonds (x=H,O,C). This joint experimental-theory project is aimed at the controlled activation of the C-H bond for the partial oxidation and oxidative dehydrogenation of methane, propane, and propene. Many oxides catalyze partial oxidation and oxidative dehydrogenation reactions but they do so only at high temperature, with low yield and poor selectivity. We intend to create novel metal oxide catalysts by using the following general strategy. Assume that an oxide, denoted generically NaOb (N is a cation, O is oxygen, and b are integers), is either inactive or activates hydrocarbons at very high temperature, with low yield and low selectivity, which makes it non competitive with the existing processes. We intend to improve its catalytic properties by creating at its surface groups of the form –O-M-O-N-O-. Here M and N are cations and O is oxygen. In what follows we call NaOb the host oxide or the host and M a metal ion dopant. Much is known about doped oxides, since dopants are used to change the electronic properties of oxides, to improve the activity of oxide-based sensors, to improve oxygen conductivity in oxide fuel cells, to increase thermal and mechanical resistance of ceramic materials or to create magnetic oxides. However, very little is known about their catalytic activity though there is some evidence that doping can improve the activity and the selectivity of the host oxide. Our aim is to use theory and experiments to explore thoroughly the extent to which this class of compounds (i.e., metal doped metal oxides) can provide useful catalysts for breaking the C-H bond in natural gas alkanes to initiate useful partial oxidation or oxidative dehydrogenation chemistry.

Platinum Group Metal (PGM) Substituted Complex Oxide Catalysts: Design of Robust Materials for Energy-Related Redox Transformations

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Funding:	$156,000

The increasing costs of platinum group metals (PGMs), arising from their scarcity, and from their ever-growing use in catalytic converters – particularly as developing countries become more stringent about automotive emissions – provides the imperative for research into better use of PGMs in catalysis. PGMs are extensively implicated in hydrogen generation from (hydro)carbon feedstocks, in the conversion of hydrogen into electricity in fuel cells, and in counter electrodes for photocatalytic water splitting. Other drivers for PGM abatement are the potential environmental impact of dispersed PGM particles, wastefully ablated from catalytic converters, and the complex geopolitics of sourcing these metals. A significant body of recent work, including from Santa Barbara, 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; inefficiencies due to only surface atoms being accessible, particle sintering with concurrent loss of active surface area, and ablation.

Our materials focus is on complex oxides; with complex implying they possess at least two crystallographically distinct cation sites. It has been clear to us that a perovskite like $BaCeO_3$, which we have explored in some detail, behaves very differently from simple oxide supports like Al_2O_3. We will explore the catalytic role/activity of PGM ions such as Pd^{2+}, Pt^{2+}, and Au^{3+} substituted in complex oxide hosts. Our specific goals are as follows:

(a) Continue to build a body of evidence pointing to the role that the substituted PGM ions in the oxide host play in catalytic oxidation, and extend our exploration to other PGM systems as well, including Rh^{3+} and Pt^{4+}.

(b) Develop 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 use them to shed light on the burning question regarding active sites: metal ion or nanoparticle?

(c) Continue our search for new hosts for PGM ions, and for new applications of the complex oxides in catalytic processes of importance to a number of processes related to energy, specifically both oxidative and reductive hydrocarbon transformations.

(d) Examine the role of electronic and ionic conductivity in the host oxide and relate it to catalytic activity.

(e) Explore thermodynamically stable oxide-on-oxide architectures such as core/shell nanoparticles, where the core is an inert oxide support and the shell around is the PGM-substituted complex oxide as a means of further optimizing the population of Pd^{2+} ions which are catalytically accessible.

The suite of test catalytic reactions that will be explored will include selective reductions (e.g., of butadiene and acetylene) and selective oxidations (e.g., propene), as well as soot oxidation, in particular, by Rh^{3+}-substituted systems. Our philosophy is one of close coupling of research and expertise in materials chemistry with surface science and catalysis.

Ring Walking/Oxidative Addition Reactions for the Controlled Synthesis of Conjugated Polymers

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Funding:	$150,000

Power conversion efficiencies of plastic solar cells depend strongly on the molecular weight characteristics of the semiconducting polymers used for their fabrication. The majority of the synthesis of these materials relies on transition metal mediated catalytic reactions. In many instances, the ideal structures cannot be attained because of deficiencies in these reactions, particularly when it comes to being able to achieve high number average molecular weights and narrow molecular weight distributions. Another important conjugated polymer structure that has yet to be attained is one in which a single functional group is attached at the end group of the chain. Such systems would be ideal for modifying surface properties at interfaces and thereby improve charge injection from the organic semiconducting layer into the metallic electrodes and in the use of these materials for labeling biomolecular probes used in fluorescent biosensors.

To respond to the challenges above, our efforts have centered on the design of homogenous transition metal complexes that are easy to prepare and effective in carrying out living, or quasiliving, condensative chain polymerization reactions. The key mechanistic challenge for the success of this reaction is to force the insertion of one monomer unit at a time via a process that involves migration of the transition metal-containing fragment to one terminus of the polymer chain. Chain growth characteristics are therefore favored when the metal does not dissociate from the newly formed reductive elimination product. We have proposed that dissociation is disfavored by the formation of a p-complex, in which the metal can sample various locations of the electronically delocalized framework, a process that we term “ring-walking,” and find the functionality where oxidative addition takes place. Success has been achieved in the nickelmediated cross coupling reaction of Grignard reagents with aromatic halides by using bromo[1,2-bis(diphenylphosphino)ethane]phenylnickel. This reagent can yield poly(thiophene)s (one of the most widely used type of polymer in plastic solar cells) with excellent stereoregularity and molecular weight distributions with polydispersities that are consistent with a living polymerization sequence. Our next objectives concern the use of these new catalysts and improved mechanistic insight in the synthesis of specific polymeric materials that demonstrate superior performance in plastic photovoltaic devices.

Early Career - Multifunctional Oxygen Evolution Electrocatalyst Design and Synthesis

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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 will 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 will 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 will use density functional theory to develop a baseline reaction energy profile for a prototype mechanism of oxygen evolution on nickel oxide. We will 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 the second basic science stage we will synthesize new high surface area, mesoporous nickel oxide and promoted oxide nanoparticle electrocatalysts using a surfactant based evaporation-induced self-assembly approach. We will probe the effect of synthesis parameters on the electrochemical oxygen evolution activity. The choice of promoters will be driven by the results found from our computational studies, and the results of the experiments will be used to validate the computational screening studies.

This project will train two graduate students and several undergraduates in energy and electrochemistry, particularly exposing them to a broad spectrum of research fields spanning atomistic simulations to applied electrochemical reactors. The computational work will create new insight into the range of opportunities to modify the activity and stability of oxygen evolution electrocatalysts through changes in structure and composition. The experimental work will provide validation for the activity predictions from the computational work and determine if higher surface area materials can increase the effective activity of electrocatalysts.

Modeling Coverage Dependence in Surface Reaction Networks

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Funding:	$112,000

The coverage of intermediates in surface reaction networks has a significant effect on the adsorption energies and reaction barriers in surface reaction networks. Neglecting or over-simplifying this coverage dependence in reaction networks can lead to serious errors in predicted rates, and can make it difficult to relate simulations to experimental data. It is, however, very difficult to quantitatively estimate the coverage dependence of these quantities because they depend on the detailed arrangements of intermediates on the surface and the interactions between them. Density functional theory (DFT) calculations can be used to calculate the coverage dependence for a small set of adsorbate configurations, but DFT is too slow and limited in system size to utilize DFT for large scale kinetic simulations. On the other hand, empirical methods for describing these interactions based on experimental data are not systematic and are often not based on a detailed atomistic description. The primary goal of this project is the development of a systematic method for describing the interactions between atoms on transition metal surfaces that accounts for the detailed atomic arrangements and is based on density functional theory calculations. This will allow us to systematically evaluate the phase behavior and the coverage dependence of the adsorption energies of these intermediates and later reaction rates on these surfaces.

At the same time we seek to understand trends in the coverage dependence of the adsorption energies of these intermediates on different metal surfaces. Density functional theory has been used to identify trends in low coverage adsorption energies on a wide range of metal surfaces. We hypothesize that these same trends exist at higher coverages. Thus, if a few metals are very well understood then the coverage dependence on other metals can be predicted from a smaller set of calculations. We plan to investigate the coverage dependence of the adsorption energies of atoms in on Pd, Ag, Au, Pt and Rh (111) surfaces using density functional theory. These initial results will examine in atomistic detail the correlations between different metal surfaces, as well as correlations between the surface electronic structure and how it changes with different coverages of adsorption on the different metals.

With a database of adsorption energies in hand, we will develop a systematic method for describing the coverage dependence that includes the detailed adsorbate configuration and is significantly faster than DFT to allow it to exhaustively enumerate the coverage dependence. The database of coverage dependent adsorption energies will be used to parameterize an algebraic function based on a cluster expansion method for each surface. The cluster expansion is in principle an exact expansion in terms of configurational basis functions in the limit of an infinite set of basis functions. In practice, we truncate the expansion and can systematically improve it by incorporation of more basis functions. The algebraic nature of the expansion makes it extremely fast to evaluate, and thus it becomes suitable for inclusion in kinetic simulations such as kinetic Monte Carlo simulations. The cluster expansion will allow an exhaustive comparison of coverage dependence on each metal surface because literally every possible configuration up to a specified size can be examined. The extent of data that will result from the proposed work is expected to dramatically increase our understanding of the interactions between oxygen, hydrogen and oxygenated intermediates on noble metal surfaces and consequently how their coverages affect reactions between them. This could be very important in understanding reactions such as the oxygen reduction reaction in fuel cells.

Molecular-Level Design of Heterogeneous Chiral Catalysts

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Funding:	$660,000

Understanding and controlling selectivity is one of the key challenges in heterogeneous catalysis. Among problems in catalytic selectivity enantioselectivity is perhaps the most the most challenging. The primary goal of the project on “Molecular-level Design of Heterogeneous Chiral Catalysts” is to understand the origins of enantioselectivity on chiral heterogeneous surfaces and catalysts. The efforts of the project team include preparation of chiral surfaces, characterization of chiral surfaces, experimental detection of enantioselectivity on chiral surfaces and computational modeling of the interactions of chiral probe molecules with chiral surfaces.

The Chiral Catalysis Group conducts a program of research on selectivity and enantioselectivity in heterogeneous catalytic surface chemistry. Selectivity has long been recognized as one of the most important characteristics of effective catalysts for complex transformations of organic species. Where such transformations can lead to multiple products, high selectivity is the key to high efficiency and waste reduction. Enantioselectivity is the ability of a catalyst to select between the two enantiomers of a chiral product; it requires the design of catalysts with chiral active sites. The Chiral Catalysis Group has identified enantioselectivity as a target of study because it represents the most subtle form of selectivity in heterogeneous catalysis. Enantioselectivity is also important in its own right for catalytic processes involving chiral reactants or products. The ongoing research program is organized conceptually around three types of enantiospecific interactions of chiral molecules with chiral catalytic surfaces: (1) interactions with naturally chiral surfaces, (2) interactions with chirally templated surfaces, and (3) one-to-one interactions of molecules with chiral surface modifiers. The program objectives include determination of the structures of chiral surfaces, elucidation of enantioselective reaction mechanisms, understanding of enantiospecific interactions of chiral adsorbates with chiral surfaces, development of methods for detection of enantiospecific surface phenomena, and preparation of chiral catalytic materials. The breadth of expertise within the Chiral Catalysis Group allows study of enantioselective catalysis at all levels ranging from molecular-scale theory to surface science to catalysis. This breadth of expertise affords a fully integrated program of research into chiral catalysis and addresses the problem of designing catalytic surfaces and active sites for selectivity control. In particular, portions of the proposed program address the problem of using organic ligands on catalyst surfaces as a means of directing selectivity in complex catalytic transformations of organic species. In addition to its impact in the field of chiral catalysis, the research program will further our general understanding of the origins of catalytic selectivity.

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

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Funding:	$640,000

This proposal presents a research plan that aims to advance the scientific foundations for heterogeneous catalysis using controlled, nanostructured materials. The proposed research program, a renewal of our existing Catalysis Science grant, will examine fundamental issues in the dynamics of model heterogeneous catalysis processes. It addresses the dynamics of both the reactants and the changing nanoparticle catalyst under reaction conditions. The program includes a strong theoretical and modeling component to examine both electronic and geometric structure, as well as reaction and vibrational dynamics. The experimental capabilities include diverse tools for inducing and probing dynamics, both on rapid time scales and with atomic-scale spatial localization. These are complemented by expertise in catalyst synthesis and testing. This program will be pursued by a team of four interacting university-based principal investigators, complemented by important collaborators in DOE and international laboratories.

The proposed research builds on significant accomplishments during the prior period. These include our ability to:

- control adsorbate motion on a microscopic scale through adsorbate/substrate interactions
- transport adsorbates by a molecular carrier
- induce and monitor surface processes on the femtosecond time scale and to follow the corresponding energy flow in nanostructured materials
- prepare and analyze nanoscale bimetallic catalyst particles with great precision
- develop realistic models of the influence of steps, defects, and the local environment on local electronic structure and reactivity

The proposed research will initially focus on the Cu/ZnO catalyst as a model system. This catalyst, which forms the basis for the well-established synthesis of methanol from syngas, presents excellent opportunities to develop a detailed understanding of the underlying dynamics, as well as the potential for optimization of the nanoscale characteristics of the catalyst. The catalyst will also form the basis for an effort to utilize photoexcitation to aid in the reduction of CO_2 to methanol. The approach will rely on photoactivated methane as the reducing agent, with the goal of achieving an efficient and thermodynamically attractive conversion of CO_2 into methanol in a process that can be carried out at low temperatures. To address the difficult problem of methane activation, we will optimize the characteristics of bimetallic catalysts derived from Cu/ZnO. In addition, the research will elucidate and attempt to improve the individual steps by which energy in incident photons is converted into C-H bond activation.

In addition to addressing the priority research direction concerning photo-induced conversion of CO_2, the planned research will support both cross-cutting challenges that were identified in the DOE Catalysis for Energy report: the characterization of solid catalysts with enhanced spatial, temporal, and energy resolution; and theory and computation for catalysis. The project's overall goals are also fully aligned with the two Grand Challenges identified in this document: (1) developing an understanding of the mechanisms and dynamics of catalyzed transformations and (2) furthering the design and controlled synthesis of catalytic structures.

Influence of the Oxidation State of Supported Size-Selected Pt Nanoparticles on Catalytic Decomposition & Oxidation of High-Order Alcohols: Activity

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To understand and engineer the next generation of nanocatalysts, a thorough understanding of the correlation between the size, shape, oxidation state and the catalytic activity is desired.

In this study the structure (size and shape) of small size-selected Pt nanoparticles synthesized by inverse micelle encapsulation has been resolved by a synergistic combination of microscopic (TEM, AFM, STM), and spectroscopic tools (X-ray absorption fine structure spectroscopy, XAFS), all integrated within a self-consistent geometric modeling method. Using micellar Pt NPs on γ-Al_2O_3 as model systems we have investigated the oxidation of 2-propanol at atmospheric pressure in a packed bed mass flow reactor for NPs with similar size but different shape. Interestingly, the lowest onset temperature for this reaction was observed for the only sample studied containing 2D NPs. This result suggest that the NP support (γ -Al_2O_3) might play a positive role in the reactivity of these NPs either by inducing strain, by providing catalytically active reaction sites at the NP/support interface (perimeter atoms), or via NP/support charge transfer processes. Nevertheless, the former sample was also the one with the highest number of low-coordinated surface atoms (e.g. edge and corner sites), which had been shown to display enhanced chemical reactivities.

To study the oxidation state effect on catalytic selectivity in situ XAFS and mass spectrometry measurements have followed the evolution of the structure and oxidation state of our 2D Pt NPs during the partial and total oxidation of 2-propanol under operando conditions. Our in situ XAFS data revealed that PtO_x species are the active phases for the partial oxidation of 2-propanol to acetone. In the complete oxidation regime, the catalysts are initially metallic, but with the surface covered by chemisorbed oxygen. X-ray photoelectron spectroscopy (XPS) measurements revealed that Pt NPs in the size range of 1-7 nm may be fully oxidized throughout their volume by exposure to an O_2-plasma treatment at RT in ultrahigh vacuum (UHV). Three distinct Pt species were found in all samples via XPS and were assigned to PtO_2 (or Pt_3O_4), PtO, and PtO. The thermal decomposition of these oxides goes as PtO_2 → PtO → PtO for all samples, including bulk Pt(111). Although PtO and PtO_2 species coexist up to ~600 K on Pt(111), the NPs show prompt decomposition of PtO_2 to PtO at lower temperatures (~350 K). PtO was found to be the most stable oxide species on the NP samples. Distinct oxide stability and NP/support interaction was observed for different supports.

Fundamental Studies of Propane Ammoxidation over Model Bulk and Supported V-Mo-Te-O Catalysts

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In 2011 to date, we performed two major studies: (1) experimental study of the microstructure of M1 phase Mo-V-Te-Ta-O catalysts and (2) theoretical studies of propane ammoxidation pathways on the M1 phase catalysts.

(1) There has been growing interest in developing highly active and selective catalysts for direct propane ammoxidation to acrylonitrile (ACN) in order to replace the current industrial technology that relies on conversion of olefins and aromatics. Mo-V-M-O (M= combination of Nb, Te, Sb, and Ta) based mixed metal oxide catalyst consisting of “M1” and “M2” phases is the most promising system among the different systems being investigated by academic and industrial research groups for the one-step propane ammoxidation. While the function and catalytic significance of Te in the structure of M1 phase catalysts have been thoroughly addressed in previous studies of the Mo-V-Te-O and Mo-V-Te-Nb-O M1 phase catalysts, the fundamental understanding of the Ta function in structurally similar Mo-V-Te-Ta-O is at present poor. We employed the aberration corrected high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and investigated the impact of the Ta incorporation in the M1 phase on the Mo/V distribution at the proposed active center and test catalytic behavior of structurally similar Mo-V-Te-Ta-O M1 catalysts in propane (amm)oxidation.

In this study, the phase pure M1 Mo-V-Te-Ta-O catalyst was prepared by two different methods, hydrothermal and microwave-assisted hydrothermal synthesis. Distribution of Mo/V cations, V-O-Ta bonds, and location of Ta at the active centers designated by Ta amount was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and HAADF-STEM. The catalytic behavior of the Mo-V-Te-Ta-O catalyst was tested in propane ammoxidation using a fixed bed micro-reaction at atmospheric pressure at 300 – 440°C. The results of this study indicated that Ta was located predominantly in crystallographic site 9 commonly described as pentagonal bipyramidal similar to that observed for chemically similar Nb cation in the M1 phase lattice. However, no differences in Ta occupancy were found as a function of distance from the M1 crystal surface contrary to results of previous studies. Lastly, the results of lattice site occupancies by the V, Mo and Ta cations were employed to predict the concentration of proposed active and selective surface sites in these catalysts which was somewhat higher than that reported recently for the structurally similar Mo-V-Te-Nb M1 catalysts. These results are in agreement with our observations of somewhat higher selectivity to C3 products (propylene+ACN) over the Ta-M1 as compared to the Nb-M1.

(2) The selective ammoxidation of propane into acrylonitrile catalyzed by the Mo-V-Te-Nb-O mixed metal oxide received considerable attention because of its environmentally friendly nature. This process consists of a series of steps involving propane oxidative dehydrogenation (ODH), ammonia and O_2 activation, and N-insertion into C3 surface intermediates. However, the limited fundamental understanding of the catalyst has hindered the progress in improving their performance required for practical applications. In 2011, we performed (1) density functional theory (DFT) calculations were performed to investigate the mechanism of propane ammoxidation over cluster models of the proposed

selective and active site present in the surface ab plane of the M1 phase. We found that vanadyl and telluryl oxo groups (V=O and Te=O) are energetically preferred by radical C3 species (isopropyl and allyl) adsorption. Meanwhile, telluryl oxo group is the strongest adsorption site for H atom and also strongest active site for hydrogen abstraction from propane. We estimated the energy barriers for propane activation on V^{5+}=O, V^{4+}=O and Mo=O sites, which indicated that V^{5+}=O is the most active site in close agreement with the experimental findings. We also explored the adsorption of NH_x (x=0-3) species and the N-insertion steps into C3 intermediates over proposed active sites present in the surface ab plane of Mo-V-Te-Nb-O M1 phase. The reactivity trends established for constituent metal cations and the information about elementary reaction steps for propane ODH found in this study are highly useful for further improvement of the M1 catalyst.

Catalyic Conversion of Glucose and Cellulose into HMF: From a Fundamental Understanding to Discrete and Recyclable Catalyst Discovery

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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.

Nanocluster Catalyst Formation and Stabilization Fundamental Studies

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The primary objective of this DOE-funded project is to follow the kinetics and establish the mechanism(s) of the nucleation and growth of supported-nanocluster heterogeneous catalysts. 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. Heterogeneous catalysts are among the most important type of industrial catalyst, but the detailed chemical events of how they form, and therefore how to better control that formation and their overall synthesis, remains an important, unsolved problem. Four specific aims are being addressed en route to answering the question of how the 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 selectivity of the catalyst. 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 that are being utilized.

The overall importance and impact of the proposed studies is that they address DOE's "Grand Challenge for catalysis science in the 21st century of understanding how to design catalyst structure to control catalytic activity and selectivity." Further details on the significance and potential impact of the proposed studies are at least 8-fold and are detailed in the original research proposal for the interested reader.

Selectivity Control Through Modification of Metal Catalysts with Organic Monolayers

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Funding:	$198,000

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.

The selective reaction of one part of a bifunctional molecule is a fundamental challenge in heterogeneous catalysis and a critically-important task for many processes including the conversion of biomass-derived intermediates. Selective hydrogenation of unsaturated epoxides to saturated epoxides is particularly difficult given the reactivity of the strained epoxide ring, and traditional platinum group catalysts show low selectivity for these reactions. In a paper published in Nature Materials, we described a new approach for the preparation of highly selective Pd catalysts involving the deposition of n-alkanethiol self-assembled monolayer (SAM) coatings. These coatings improve the selectivity of 1-epoxybutane formation from 1-epoxy-3-butene on palladium catalysts from 11% to as high as 94% at equivalent reaction conditions and conversions. Although sulfur species are generally considered to be indiscriminant catalyst poisons, we find that the reaction rate to the desired product on a catalyst coated with a thiol having an 18 carbon aliphatic tail was 40% of the rate on an uncoated catalyst. Interestingly the activity decreased for catalysts coated with less ordered SAMs having shorter chains. The behavior of SAM-coated catalysts was compared to catalysts where surface sites were modified by carbon monoxide, hydrocarbons, or sulfur atoms. The results suggest that the SAMs restrict sulfur coverage to enhance selectivity without significantly poisoning the activity of the desired reaction. We have recently found that SAMs can furthermore be employed in liquid-phase reactions to control selectivity by modification of surface-solvent interactions.

In a separate study recently published in Langmuir, we conducted surface-level investigations of the adsorption of EpB and related molecules on SAM-coated Pd(111), with an aim of identifying mechanistic explanations for the observed catalytic behavior. Alkanethiol SAM-covered Pd(111) surfaces were prepared by conventional techniques and transferred to ultrahigh vacuum, where they were characterized using Auger electron spectroscopy (AES) and temperature programmed desorption (TPD) of EpB and other probe molecules. Whereas previous studies have shown that EpB undergoes rapid decomposition via epoxide ring opening on uncoated Pd(111), TPD studies show that EpB does not undergo substantial ring opening on SAM-covered surfaces, but rather desorbs intact at temperatures less than 300 K. Systematic comparisons of EpB desorption spectra to spectra for other C4 oxygenates suggest that the SAM creates a kinetic barrier to epoxide ring-opening reactions that does not exist on the uncoated surface. The EpB desorption spectra as a function of exposure show behavior similar to the desorption of olefins from Pd(111), indicating that the binding of the olefin functionality, in contrast to that of the epoxide ring, is not significantly perturbed. EpB desorption spectra from surfaces with less well-ordered SAMs show the presence of weakly bound states not observed on well-ordered SAM surfaces. The lower activity observed on catalysts covered with less well-ordered SAMs is hypothesized to occur due to partial confinement of adsorbates into these weakly bound, less active states.

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

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We are trying to replace the stoichiometric use of trialkyltin hydrides in radical chemistry with the catalytic use of transition-metal hydrides. Our catalytic cycle requires the regeneration of such hydrides with H_2 from the corresponding metalloradicals. We are examining the ability of cobalt dimethylglyoxime complexes to split H_2, to transfer H•, and to cyclize appropriate substrates catalytically.

We have found that $Co(dmgBF_2)2(OH_2)2$ and $Co(dmgBF_2)2(CH_3CN)2$ are excellent catalysts for radical cyclizations under H_2. We believe that these Co complexes form hydrides under H_2 gas, and are using (p-$tBuC_6H_4$)3C• to remove H• from these hydrides as soon as they are formed. The overall reaction, in which two equivalents of (p-$tBuC_6H_4$)3C• and one of H_2 are converted to two equivalents of (p-$tBuC_6H_4$)3CH, appears to be independent of (p-$tBuC_6H_4$)3C•, first order in H_2, and second order in Co. In collaboration with the Inorganic Photochemistry group at Brookhaven National Labs (which has appropriate high pressure UV-vis equipment) we are examining the reaction of $Co(dmgBF_2)2(OH_2)2$ with H_2 in the absence of added radicals.

We are also studying the ability of transition-metal hydrides to transfer H• to alkynes. We have found that CpCr(CO)3H hydrogenates phenylacetylene through a radical mechanism. We have been able to use H• transfer to an aryl acetylene to effect the cyclization of a 1,5 eneyne. We are studying H• transfer to other alkynes (dimethyl acetylenedicarboxylate, methyl propiolate, etc.).

Finally, we are studying the the ability of transition-metal hydrides to transfer H• to vinyl ethers.

Catalytic Methods to Form Organic Electronic Materials

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Funding: $170,000

This grant has two broad objectives: (1) synthesize and study hemispheric molecules and (2) 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.

Bowl-shaped aromatics form the basis for one portion of this grant. We will develop the catalytic methods to convert these bowl-shaped hydrocarbons into hemispheres and these hemispheres into carbon nanotubes. It would be the first hemispheric form of carbon to have been formed deterministically. We intend to study these molecules in the context of their properties as electronic materials and in host-guest complexes with fullerenes. In addition, we will explore the reactivity of such hemispheres as a means to synthesize carbon nanotubes with a priori defined diameters and chiral twist angles.

We will utilize living alkyne and alkene metathesis polymerization reactions as a means to produce molecular wire precursors. These polymers form the basis for the second portion of this grant because we intend to develop the catalytic tools to convert them into ribbons of graphene. These ribbons would have their width atomically defined and their length defined by a living polymerization process. These ribbons would find immediate application as high performance organic electronic materials and would drive many physical inquiries. These materials will be tested in thin film and single molecule electronic devices.

The importance to DOE 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.

Fundamental Studies of Metal Centered Transformations Relevant to Catalysis

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The specific objectives and research goals of the research performed during the present grant period have been to obtain information that is relevant to transition metal mediated transformations of organic substrates. Such studies are of importance due to the fact that vast quantities of organic materials are available from natural resources, but their full potential is yet to be realized because of synthetic difficulties. Specific issues that were addressed during the course of this research included (1) coordination chemistry of molybdenum relevant to hydrodeoxygenation; (2) the *tris*(2-mercapto-1-t-butylimidazolyl)hydroborato ligand, [$\mathrm{Tm}^{\mathrm{Bu^t}}$], to prepare sulfur-rich counterparts of metallocenes; (3) a new class of reactivity of $W(PMe_3)_4(CH_2PMe_2)H$ that results in the formation of the alkylidene cation, $[W(PMe_3)_4(CHPMe_2)H]^+$; and (4) the development of a [*CCC*] X_3 pincer ligand for early transition metals.

Hydrodeoxygenation (HDO) is the industrial process by which oxygen-containing species are removed from crude petroleum feedstocks. Although this process has received less attention than hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) because (1) the combustion of oxygen-containing compounds does not pose an environmental problem and (2) the amount of oxygen present in crude oil is sufficiently small that it does not significantly mar fuel performance, it is becoming increasingly important as the availability of light petroleum feedstocks dwindles and attention turns to biomass and heavier fossil feedstocks, such as heavy oils, tar sands, oil shale and coal. Specifically, the oxygen content of the synthetic crude oils derived from these sources is sufficiently high that HDO is essential for obtaining useful fuels; for example, the oxygen content of bio-oil (35 – 40 wt %) is such that the energy content is approximately half of that of petroleum. Efforts to improve the efficiency of HDO would benefit greatly from a molecular level understanding of the means by which the various oxygen-containing species interact with metal centers and, for this reason, we have investigated the reactivity of furans, a class of oxygen-containing molecules for which the coordination chemistry is poorly developed and which are most resistant to HDO. In particular, we have focused on the reactivity of furans towards electron-rich compounds of molybdenum and tungsten.

Significantly, we have discovered that $Mo(PMe_3)_6$ and $Mo(PMe_3)_4H_4$ cleave the C–O bond of furan to give butadiene-alkoxide and carbonyl complexes. The formation of these carbonyl complexes and propene is of most significance because it indicates that the molybdenum complexes are capable of breaking both C–O and C–C bonds of furan which mimics the observed dissociation of furan into CO and propylene on a molybdenum sulfide catalyst surface.

Cyclopentadienyl ligands have played an important role in the development of organometallic chemistry, as exemplified by the metallocene systems and their use as olefin polymerization catalysts. Electronically related to cyclopentadienyl are C_3 symmetric L_2X tripodal ligands and we have therefore introduced the use of *tris*(2-mercapto-1-t-butylimidazolyl)hydroborato ligands in zirconium chemistry. For example, we have synthesized the zirconium benzyl compound $[Tm^{But}]Zr(CH_2Ph)_3$ and the mixed sandwich complex $Cp[Tm^{But}]ZrCl_2$.

$W(PMe_3)_4(CH_2PMe_2)H$ has been employed in a variety of bond activation reactions in which the reactivity is generally interpreted in terms of a pre-equilibrium with the 16-electron complex $[W(PMe_3)_5]$. It is, therefore, significant that we have discovered a new reaction manifold that involves the overall formal abstraction of hydride from the CH_2 group of the cyclometallated PMe_3 ligand. Specifically, $W(PMe_3)_4(CH_2PMe_2)H$ reacts with aryl halides to give the alkylidene complex, $[W(PMe_3)_4(CHPMe_2)H]^+$. Furthermore, treatment of $[W(PMe_3)_4(CHPMe_2)H]^+$ with $LiAlD_4$ gives selectively $W(PMe_3)_4(CHDPMe_2)H$, in which the deuterium resides in the methylene group, and subsequent migration of deuterium provides a means to measure the rate constant for the formation of the 16-electron species $[W(PMe_3)_5]$ from $W(PMe_3)_4(CH_2PMe_2)H$.

A new class of [*CCC*] X_3-donor pincer ligand for transition metals has been constructed *via* cyclometalation of a 2,6-di-*p*-tolylphenyl ($[Ar^{Tol2}]$) derivative. Specifically, addition of PMe_3 to $[Ar^{Tol2}]TaMe_3Cl$ induces elimination of methane and formation of the pincer complex, $[Ar^{Tol'2}]Ta(PMe_3)_2MeCl$ (Tol' = C_6H_3Me), which may also be obtained by treatment of $Ta(PMe_3)_2Me_3Cl_2$ with $[Ar^{Tol2}]Li$. Deuterium labeling employing $Ta(PMe_3)_2(CD_3)_3Cl_2$ demonstrates that the pincer ligand is created by a pair of Ar–H/Ta–Me sigma-bond metathesis transformations, rather than by a mechanism that involves alpha–H abstraction by a tantalum methyl ligand.

Porous Nano-size Metal Oxides, Synthesis, Catalysis

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The goals of this project are to prepare and characterize porous nano-size metal oxide systems for activation of carbon dioxide, water, and selective oxidations. DOE Interest in this project concerns development of a fundamental understanding of the mechanisms of selective catalytic oxidations is important in the areas of energy and catalysis. Selective catalytic oxidations, activation of carbon dioxide, solar photocatalysis, novel batteries and electrocatalysis are areas being pursued. Porous nano-size metal oxides are useful in these green applications. Redox catalysis, electron and energy transfer, mixed valency, mechanistic studies, characterization of molecular transformations, and detailed knowledge of structure are controlled to improve energy efficiency in these reactions. One area involves synthesis of nano-materials. The focus of our synthetic work involves novel syntheses and phases, new morphologies, and framework substitutions. Metal and mixed metal oxides of manganese, titanium, copper, zinc, iron, and mixed metal systems have been the focus of this work. Unique ultrathin materials, controlled morphologies of various nano-size metal oxides, and control of particle sizes have been realized. Pore size and hydrophobicity control have been used.

Characterization Studies have involved In situ X-ray powder diffraction (XRD), In situ synchrotron XRD, adsorption, electron microscopy, soft XPS, X-ray absorption, infrared, Raman, thermal, chemical analysis, and other methods have been used to study the above systems after synthesis, after reaction and in situ during catalytic reactions. Synchrotron work is being done at Brookhaven National Labs. Catalytic studies concern all materials described above that have been studied in various catalytic reactions. Selective oxidations of various substrates with oxygen or with peroxides, photocatalytic degradations of toxic species, activation of carbon dioxide, improved battery and fuel cell catalysts, fuel reforming, and other reactions have been studied. Evidence of catalytic redox cycling, multifunctional catalysis, morphological effects in catalysis, hydrophobic effects on catalytic reactions, catalytic intermediates, and other phenomena have been observed with these systems. Out future work entails studies of efficient activation of carbon dioxide, degradation of toxic species, control of pore sizes, and understanding the role of morphology in selective catalytic reactions.

Understanding the Effects of Surface Chemistry and Microstructure on the Activity and Stability of Pt Electrocatalysts on Non-Carbon Supports

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The objective of this project is to elucidate the effects of the chemical composition and microstructure of the electrocatalyst support on the activity, stability and utilization of supported Pt clusters. Advances in fundamental understanding in this area has the potential to have a significant impact on the performance and durability of several devices. In this work, the PI will focus on electrochemical applications, most notably the electrocatalyst systems for the oxygen reduction reaction (ORR) in the proton exchange membrane fuel cell (PEMFC). However, the findings of this study can impact heterogeneous catalysis in general, where catalyst-support interactions are of great interest. In this work, four hypotheses will be tested:

(1) The electrocatalytic activity of nanosized Pt clusters can be enhanced by tailoring the metal-support interaction between the Pt catalyst and the catalyst support material.

(2) Increasing the interaction between the nanosized Pt clusters and the support material will increase Pt cluster stability.

(3) The microstructure of non-carbon catalyst supports can be tailored to increase both the electrochemically active area and reactant mass transport.

(4) An electrochemically modified Thiele modulus can be used as a predictive design tool for supported Pt electrocatalysts.

A combined experimental and theoretical approach will be used to test the hypotheses. Four catalyst support materials will be considered in this study: (1) highly ordered mesoporous carbon (HOMC), (2) tungsten carbide (WC), (3) indium tin oxide (ITO), and (4) titanium aluminum nitride (TiAlN). Nanosized Pt clusters will be deposited on each catalyst support. Each supported electrocatalyst will be exposed to a series of electrochemical and materials analysis techniques. Concurrently, theoretical calculations will be utilized to shed light on the effect of the catalyst-support interaction on the electronic configuration of Pt clusters and a microporous catalyst transport model, utilizing an electrochemically modified Thiele modulus used to guide the design of high surface area electrocatalysts.

During the first year of the project, we had two specific aims. Our first aim was to synthesize and both physically and electrochemically characterize high surface area WC and TiAlN. Our second aim was to modify our existing self-assembled template technique and prepare templates with different pore sizes. In both regards, we have been quite successful.

Aim 1: High surface area WC supports were successfully prepared using a molten solvent technique and extensively characterized both physically and electrochemically. For platinum supported on WC (Pt/WC) the team found (1) the electrocatalytic activity of Pt clusters is enhanced for the ORR on Pt/WC compared with conventional Pt/C; (2) small, well dispersed Pt clusters can be obtained on WC, even at high loadings; (3) during electrochemical treatment at potentials relevant to the ORR, WC is converted to a less conductive WO_3; and (4) the formation of WO_3 facilitates the high surface mobility and detachment of Pt clusters from the surface, which limits the ORR activity enhancement of these catalysts to short times and results in large Pt clusters after cycling. For the TiAlN support, as of the date of this report, the team has developed a synthesis schedule, assembled a custom chemical vapor deposition reactor and ordered MgO substrates for deposition.

Aim 2: The team has developed a method of additive deposition for the preparation of template materials with average pore sizes between 8 and 15 nm with a very narrow distribution (< 1 nm at ½ width). This has been used to prepare highly ordered mesoporous carbon supports with varying physical characteristics, which has yielded an improvement in the observed ORR performance for the supported Pt clusters due to increased oxygen mass transport in the structure. The selected electrolyte also plays a significant role in its electrochemical response.

Chemical Imaging of Single Metal Nanoparticle Catalysis

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Funding:	$160,000

Catalysis is a key technology in meeting the increasing energy demands of the United States and the world. Realizing the full potential of catalysis requires understanding the properties of catalysts at varying time and length scales. Many scientific challenges exist, however, in characterizing catalysts, especially for nanoparticle catalysts that differ from one particle to another and that have diverse catalytic sites on their surfaces. New tools are needed to make high spatial resolution measurements of operating nanoparticle catalysts, preferably in real time at realistic reaction conditions.

Prof. Peng Chen's group at Cornell University has developed a single-molecule fluorescence approach to study the real-time catalysis of metal nanoparticles at the single-particle level and single-turnover temporal resolution under ambient solution conditions. By detecting a fluorescent catalytic product, they were able to image the catalytic reactions one event at a time on a single nanoparticle. Initially focusing on Au-nanoparticle catalysts, they have gained fundamental insight into the intricate interplay between heterogeneous reactivity, differential selectivity, dynamic surface restructuring, and variable surface sites in nanocatalysis.

Many compelling questions still remain. For example, can one spatially resolve catalysis to sub-particle resolution on a single-particle so one can directly identify what surface sites are responsible for catalysis? And, can one study more application-relevant catalysts besides Au-nanoparticles with the single-molecule approach? In this proposal, Chen lays out two research projects to address these questions. In the first project, they apply super-resolution optical imaging methods to spatially resolve catalysis on a single Au-nanoparticle down to nanometer resolution, building on their success in single-molecule imaging of nanoparticle catalysis. They 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, they extend their single-molecule studies to one of the most important industrial catalysts, Pt-nanoparticles, in particular shaped-controlled Pt-nanoparticles; Chen also outlines plans to pursue more catalytically relevant chemical transformations. They 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 will provide unprecedented spatial and temporal information on the catalytic properties of nanoparticle catalysts. The knowledge obtained will help us understand the fundamental principles governing the catalytic properties of nanoscale catalysts, contributing to the efforts in meeting society's energy challenge.

Development and Application of Carbonylation Catalysts for the Synthesis of Biodegradable Polymers

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Funding:	$160,000

The goal of this research proposal is the development of new catalysts for heterocycle carbonylation. The project focuses on three main objectives: (1) the development of a new generation of heterocycle carbonylation catalysts with improved activities and selectivities, (2) the application of heterocycle carbonylation catalysts to access high-value organic synthons and to synthesize monomers for unique polymer architectures, and (3) the study of the mechanisms of heterocycle carbonylation in a range of fundamentally new catalytic transformations. These objectives are interrelated, such that success in any one area leads to innovation and understanding across all three.

In the last funding period, significant advances were made in understanding the detailed catalytic mechanisms of epoxide and lactone carbonylation. On the basis of these results, new catalysts with improved properties were developed. Three of these catalysts are now commercially available through the Aldrich Chemical Company. In addition, the application of these catalysts for the carbonylation of other heterocycles was initiated.

The proposed work focuses on the development of a new set of catalysts that addresses a group of diverse challenges. General areas of focus in the proposed studies include enantioselective carbonylation catalysts, catalysts that enhance the rate of double carbonylation of epoxides to succinic anhydrides, systematic variation of the metal-carbonyl and Lewis acid portions of the catalysts, and supported catalysts that will facilitate recycling and catalyst removal. We are also exploring new applications for our family of bimetallic carbonylation catalysts, while maintaining our focus on efficient catalytic reactions for the production of both useful monomers and synthetically relevant, bioactive molecules. Finally, we will undertake studies to fully understand the detailed mechanisms of new heterocycle carbonylation catalysts.

The key benefits of this work extend well beyond the development of new carbonylation catalysts. The energy-efficient synthesis of environmentally benign materials from renewable resources will be increasingly important as the availability of fossil fuels diminishes. The proposed carbonylation catalysis offers an effective approach, as CO can be derived from biomass and the reactions operate under mild conditions. In addition, we plan to develop catalytic heterocycle carbonylations that will allow the efficient synthesis of a range of fine chemicals as well as pharmaceutical intermediates. Finally, we believe that the continued pursuit of a precise mechanistic understanding of these heterocycle carbonylation catalysts will have an important impact in a much broader context on the field of catalysis.

Catalysis of Small Molecule Activation by Proton Coupled Electron Transfer

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Funding:	$160,000

The objective of this project is the catalysis of proton coupled electron transfer (PCET) to metal bound fragments derived from the most abundant small molecules (i.e., O_2 and N_2). There are many important chemical challenges that are tied to this fundamental reaction. Among these are metal catalyzed oxidations of organic molecules utilizing O_2 as the oxidant; reduction of O_2 to water close to the thermodynamic potential, i.e., the cathode of any fuel cell based on reactions with O_2; fixation of nitrogen at modest temperatures and pressures; and transfer of reduced nitrogen species to organic substrates.

Any one of these problems has obvious implications for the generation and/or utilization of energy on a large scale.

The realization that a hydrogen atom abstraction [e.g., an elementary step occurring during the course of metal-catalyzed hydroxylations (RH -> ROH) or aminations (RH -> RN(R)H)], must be considered a PCET process brings into focus the broader issue of the synchronous delivery of protons and electrons to metal bound atoms and molecules. The conceptual separation of H^+ and e- and their respective sources and destinations leads directly to a consideration of redox-active ligands, and the role they might play in facilitating PCET processes. One of the facets of the proposed research is to create metal complexes with redox-active functional groups, and thereby functionally mimicking metalloenzymes with electron transfer sites.

The methods employed involve the synthesis and characterization of coordination compounds of various transition metal (Cr, Fe, Co) as well as the study of their reaction mechanisms. We will use tridentate tris(pyrazolyl)borate (‘Tp’) and bidentate b-diketiminate (‘nacnac’) ligands; whereas the former tend to stabilize reactive intermediates the latter will enable closer contacts between reactive species and external substrates. The diversity in accessible coordination geometries will create opportunities for new chemistry. Redox-active versions of these ligands will facilitate PCET processes. Benefits of this research include the potential discovery of new catalytic processes and the advancement of fundamental knowledge about chemistry and catalysis.

Dedicated Beamline for Catalytic Research - Synchrontron Catalysis Consortium (SCC)

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Funding: $300,000

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 XRD
- Dedicated 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

These tasks will be performed by a consortium consisting of PIs and co-PIs from academic, national, and industrial laboratories. The beamlines and facilities are located in the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratories. The PIs and co-PIs have extensive experience in the areas of catalysis, electrocatalysis, advanced materials, and synchrotron spectroscopies. The combined expertise of the team members will create the synergy that is necessary to assure the success of the dedicated beamline facilities for catalytic research. The SCC members will also devote significant efforts to assure that catalysis interests and needs are addressed in NSLS II.

From First Principles Design to Realization of Bimetallic Catalysts for Enhanced Selectivity

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Funding: $680,000

The goal of this project is to demonstrate a new paradigm for 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. In this funding period, now alkali-metal promoted, Pt-based low-temperature Water-Gas-Shift catalysts have been reported in *Science* by the Mavrikakis group and collaborators. Highly selective Pd/Ag bimetallic catalysts for ethylene epoxidation were discovered and reported by Barteau and Lauterbach groups. In a report soon to be published, Barteau and Lobo have established the reaction network for the decomposition of propylene oxide surface intermediates during the propylene epoxidation reaction. This information has been the basis for the discovery of selectivity enhancements in the reaction by the addition of small amounts of butadiene.

New methods for the preparation of uniform Ni-Pt bimetallic nanoparticles were reported by the Chen and Lauterbach's groups that will be used to develop heterogeneous catalysts that incorporate discoveries from surface science from Chen's group. Vlachos group has develop a novel group-additivity scheme for reactions on metal surfaces that we believe will be of great value to the catalysis community in general in the development of better catalysts. These results 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.

Novel Photocatalysts With One- and Two-Dimensional Nanostructures

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Funding: $175,000

We have discovered new semiconductor photocatalysts that use visible light to promote photooxidation of organic molecules in the gas and liquid phases. We have used a combination of experimental and theoretical methods to understand the electronic structure of these new materials and identify the key variables that control the formation of electrons and holes upon photoexcitation. The new materials are more effective using visible light for photocatalysis than the conventional anatase TiO_2-based photocatalyst. Theory has been fundamental to guide experiments toward 'ideal' compositions that are realizable within a particular crystalline phase. These materials have been prepared using sol-gel-derived precursor oxides that mix at the molecular level d0 (TiIV) and d10 (GaIII, ZnII, GeIV and SnIV) metal cations and facilitate the formation of novel crystalline phases. Photocatalytic studies in the presence of electron and hole scavengers have been used to identify the kinetically relevant mechanisms of photo-oxidation on the different catalysts. We find that on the same photocatalyst, the most important reaction paths depend on the organic moiety that is oxidized. These materials could be used for the photodecomposition of undesirable organic compounds using natural or artificial visible light.

Structure-Property Relationship in Metal Carbides and Bimetallic Alloys

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Funding:	$135,000

The main objective of the current DOE-sponsored research is to correlate the structure-property relationship in metal carbides and bimetallic alloys, with an aim at replacing or substantially reducing the loading of Pt-group metals in catalysts and electrocatalysts. It is well known that the electronic and catalytic properties of transition metals can be modified by alloying either with carbon to form carbides or with another metal to produce bimetallic alloys. The carbide and bimetallic materials are therefore excellent model systems to demonstrate the feasibility of tuning the catalytic activity, selectivity, and stability, which should help identify carbide and bimetallic materials as alternatives to replace Pt-group metal catalysts.

The primary objective of the current research is to further unravel the structure-property relationship in carbide and bimetallic catalysts, with a special focus on the fundamental understanding of ways to improve the activity, selectivity and stability of these catalysts by anchoring bimetallic catalysts on carbide substrates. In the area of catalytic activity, we will use the hydrogenation of C=C and C=O bonds in unsaturated hydrocarbons, 1-butene, 1,3-butadiene and acrolein, to determine the possibility of enhancing the activity by anchoring bimetallic catalysts over carbide substrates. In the area of catalytic selectivity, we will use the reforming of oxygenates, methanol and ethylene glycol, as probe reactions to control the bond scission sequence of C-H, O-H, C-O and C-C bonds from the synergistic interaction of metal monolayer on carbide substrates. In the area of catalytic stability, we will investigate how the anchoring of the Pt-3d-carbide “sandwich” structure would improve the segregation kinetics of the subsurface 3d atoms with adsorbed oxygen, such as in the cathode environment in PEM fuel cells. If successful, the proposed research would demonstrate the feasibility of rational design of novel materials with enhanced catalytic properties, which would have significant impact in DOE programs in the areas of fundamental catalysis and electrocatalysis.

Principles of Selective 02-Based Oxidation by Optimal (Multinuclear) Catalytic Sites

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Funding:	$240,000

GOALS

(A) 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.

(B) 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.

(C) Develop an innovative computational methodology that enables the understanding of the mechanisms and dynamics of catalytic reactions involving multi-center transition-metal catalysts.

RECENT ACTIVITIES

(A) We developed a homogenous water oxidation catalyst (WOC) based on earth-abundant elements, $Na_{12}[Co_3(H_2O)_2W(CoW_9O_{34})_2]$ (1). With $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) as a photosensitizer and persulfate as a sacrificial electron acceptor, we observed for 1 at pH 9 a turnover number (TON) $>10^3$ at remarkably low concentrations (0.1-0.5 μM) of 1. The O_2 yield based on persulfate is up to 42%, and the estimated turnover frequency (TOF) is $\approx 10^2\ s^{-1}$.

(B) We prepared a homogeneous catalyst $Na_{10}[Co_4(H_2O)_2(VW_9O_{34})_2]$, 1_V2, that keeps the oxidatively and hydrolytically robust structure of 1_P2 (reported earlier) but is by far the fastest WOC to date. We directly compared the catalytic efficiency of 1_V2 and 1_P2 for water oxidation. It was found that the apparent TOF (TOF_{app}) of 1_V2 is $3.7 \times 10^2\ s^{-1}$, which indicates that 1_V2 is *ca.* 16 times more reactive than 1_P2 in dark water oxidation.

(C) We thoroughly studied the stoichiometric oxidation of alcohols by $[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$, (2). The reaction proceeds in two steps, a relatively fast one-electron reduction of 2, followed by a slower second one-electron reduction step. Re-oxidation of thus reduced Ru_4-POM by dioxygen is very slow process.

(D) We elucidated the mechanisms of water oxidation by 2 and shown that it would proceed via "direct O-O bond formation" pathway.

(E). We continued our efforts on fitting and testing a "reactive" force field on simple systems such as the Lindqvist POMs, formula: $M_6O_{19}^{n-}$, where M = Mo, W, Nb and Ta, and the γ-M_2-Keggin POMs (where M = Co and Ru). The ReaxFF parameters for the Nb_6 and Ta_6 Lindqvist ions were integrated into the TINKER suite of MD codes and used to model POM solvation dynamics at various levels of pH.

Growth and Reactivity of Oxide Phases on Crystalline Pd and Pt Surfaces

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Funding:	$200,000

The main goals of our project are to elucidate the mechanisms governing the oxidation of crystalline Pd and Pt surfaces, and to advance the fundamental understanding of the reactivity of the resulting oxide phases. We are focusing particularly on characterizing mechanistic aspects of alkane adsorption and chemical transformations on a PdO(101) thin film. This effort is motivated largely by the need to develop more efficient methods for utilizing alkanes as fuel sources and also as feedstocks for chemical production.

During FY 2011, we investigated the adsorption and reactions of n-butane, methanol, carbon dioxide and several propane isotopologues on PdO(101). Our investigations have clarified the nature of alkane sigma-complexes which form on the PdO(101) surface and the key role that these adsorbed species play in mediating initial C-H bond activation. By conducting experiments with several propane isotopologoues, we discovered that the initial activation of propane sigma-complexes on PdO(101) occurs with high selectivity (~90%) by cleavage of a primary C-H bond. This study appears to be the first to report a strong preference for primary C-H bond cleavage of an alkane on any solid surface. In our study of methanol oxidation on PdO(101), we found that the oxidation selectivity shifts from favoring complete to partial oxidation to methyl formate as the initial methanol coverage increases. This finding may have implications for understanding factors which determine the oxidation selectivity of alkanes and other molecules on Pd oxide surfaces.

In conjunction with experimental studies, we have also been using quantum chemical calculations to investigate the surface chemistry of PdO(101), and have focused particularly on utilizing a dispersion-corrected density functional theory method known as DFT-D3. We find that calculations using the DFT-D3 method quantitatively reproduce the measured binding energies of n-alkanes on PdO(101) and Pd(111) as well as the binding of CO_2 on PdO(101) over a wide range of CO_2 surface coverages. Initial results show that the DFT-D3 calculations also provide accurate estimates of C-H bond activation barriers for alkanes on PdO(101), including correctly predicting the preference for primary versus secondary C-H bond cleavage of propane on this surface.

Finally, we investigated structural changes that occur during the thermal decomposition of PdO(101) thin films using scanning tunneling microscopy (STM). These experiments reveal strong spatial anisotropies in the decomposition kinetics which produce aggregates of reduced sites, such as chains and loops of Pd adatoms as well as the regeneration of oxide domains at the surface due to atom exchange between the bulk and surface of the decomposing film. These findings provide new insights for understanding microscopic processes that occur during the reduction of thin film oxides.

In-Situ NMR/IR/Raman and Ab Initial DFT Investigations of Pt-Based Mono- & Bi-Metallic Nanoscale Electro-Catalysts: From Sulfur-Poisoning to Polymer

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Funding: $170,000

This project targets two primary objectives: (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. (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 (Ef –LDOS), and the associated electrochemical reactivity. For achieving these objectives, we propose to use surface 195Pt and 13C of chemisorbed 13CO 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 195Pt and 13C NMR have been proven unique in measuring the Ef –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 119Sn, 109Ag, 103Rh, or 207Pb) 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. The expertise and major equipments for carrying out the proposed research are already in place in the PI's laboratory.

Although of great practical and fundamental importance in improving impurity tolerance of electrode materials for low and high temperature hydrogen fuel cells, systematic fundamental investigations of sulfur-poisoning of practical Pt-based electrocatalysts in an electrochemical environment and its possible remedies have been surprisingly rare. A non-exhaustive literature search that included the recent DOE's annual reports of DOE-supported projects has turned up only a few relevant papers/reports and most (if not all) of which were at a primordial level of surveying and assessing poisonous effects of impurities such as H_2S, SO_2, NH_3, and NO_2, etc. on the performance of fuel cells. Therefore, as assessed in the Feb 2004 OBES report, "Basic Research Needs for the Hydrogen Economy," detailed fundamental studies of the sulfur poisoning of electrode materials have yet to be undertaken. Consequently, our current insufficient electronic-level understanding of the problem represents an urgent contemporary challenge in the basic research supported by DOE-BES. The proposed research is intended to fill in such a void and provide rich benchmark data urgently needed for achieving a broad-range mechanistic understanding of the sulfur poisoning and for critically assessing and further developing quantum theories of (electro)catalytic reactivity. The anticipated great stride brought to bear by this project on our fundamental understanding of the sulfur poisoning will facilitate the design and development of new impurity-resistant Pt-based electrocatalysts which will in turn contribute in a significant way to the development of more sustainable and reliable fuel cells.

Developing the Science of Immobilized Molecular Catalysts

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Funding: $700,000

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

Understanding the Interfacial Structures - Chemistry Relationships in Solid Oxide Fuel Cells (SOFC)

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Funding: $80,000

New anode materials of Ni-BaZr0.1Ce0.7Y0.2-xYbxO3-d have been developed for solid oxide fuel cells. The mixed ion conductor, BaZr0.1Ce0.7Y0.2-xYbxO3-d, exhibits high ionic conductivity at relatively low temperatures (500° to 700°C), which allows rapid transport of both protons and oxide ion vacancies. The new anode shows excellent tolerance to coking and sulfur poisoning. The ability to resist deactivation by sulfur and coking appears linked to the mixed conductor’s enhanced catalytic activity for sulfur oxidation and hydrocarbon cracking and reforming, as well as enhanced water adsorption capability.

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

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Funding:	$180,000

The goal of this project is to develop a molecular-scale mechanistic framework for complex selective oxidation processes on gold and gold-based alloys as a means of understanding how to improve selectivity and activity of catalyst materials that can operate at low temperature by bridging model studies on extended gold surfaces and working gold catalysts. Heterogeneous catalysis is a key technology for securing our future because most major chemical syntheses rely on heterogeneous catalysis to control activity and selectivity. Gold is an attractive catalyst because it is highly active and very selective for partial oxidation processes suggesting promise for energy-efficient “green” chemistry. Fundamental understanding of reaction mechanisms is an important step to designing new materials and processes for important catalytic reactions.

We have combined theory and experiment to understand selective oxidation reactions on Au because of the intense recent interest in using gold to promote reactions with high selectivity and at low temperature. Our recent significant accomplishments are (1) bridging the gap between model surface chemistry investigations and a catalytic process at atmospheric pressure for selective oxidation of alcohols catalyzed by gold; (2) building on our understanding of the molecular-scale mechanisms for alcohol and olefin oxidation, to understand how to control selectivity for complex cross coupling reactions promoted by metallic gold; and (3) discovering and demonstrating new classes of reactions promoted by O-covered metallic Au that will motivate the study of new catalytic processes. We have made an unprecedented connection between our fundamental mechanism at low pressure and implementation under catalytic conditions.

Model studies show that atomic oxygen bound to metallic Au in 3-fold sites has high activity the oxidation of methanol. Our model studies showed that (a) adsorbed O is required for O-H dissociation to form methoxy; (b) dissociation of the C-H bond to form formaldehyde occurs subsequently in the rds and can be promoted by adsorbed O, OH or another methoxy; (c) reaction between residual methoxy and formaldehyde to form $CH_3OC(H_2)=O$ is essential barrierless and diffusion of these reactants on the surface is facile; and (d) elimination of H yields methyl formate, the selective oxidation product.

In parallel studies of methanol oxidative coupling on nanoporous gold we achieved near 100% selectivity for methyl formate production using O_2 as an oxidant and a total pressure of 1 atm. Selective oxidative coupling was promoted even at room temperature and the activity is retained for at least 14 days. The trends in selectivity control as a function of O_2 partial pressure are in agreement with our model studies—at higher concentrations of oxygen and at higher temperature, there is more combustion.

We have built on our understanding of the molecular-scale steps for complex, selective olefin oxidation and alcohol oxidative coupling over oxygen-covered Au(111) to establish fundamental principles governing selectivity in complex systems. Recent focus has been on oxidative coupling of mixtures of alcohols and the selective oxidation of substituted olefins that contain allylic C-H bonds.

A significant accomplishment of our work is the generalization to predict new synthetic pathways promoted by oxygen-covered Au. Two classes of reactions were predicted and experimentally confirmed in our lab: (1) the low-temperature activation of the N-H bond in secondary amines to yield R_2N(ads), which attacks the C in formaldehyde when it is introduced to the surface yielding $R_2NC(H)=O$, and (2) carbonylation of methoxy to yield $CH_3O-C(=O)OCH_3$. These examples illustrate the value of fundamental understanding of reaction mechanisms as a means of rationally predicting new pathways for producing these commodity chemicals.

Development of Catalytic Alkylation and Fluoroalkylation Methods

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Funding:	$145,000

The overall goal of this project is to develop new synthetic methods that are both energy efficient and broad in scope for introducing alkyl and perfluoroalkyl groups into organic molecules. Developing selective methods to cross-couple alkyl groups has important synthetic value as these types of linkages are expected to be pervasive in newly designed organic molecules and materials. The research described in this proposal outlines a program 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 traditional metals such as palladium. The proposed research focuses on using cheap, readily available, and environmentally benign metals in efforts to overcome technical obstacles and to make the new methods as universal as possible.

It was first reported by us in 2004 that terpyridine nickel complexes can catalyze the cross-coupling of alkyl halides with alkyl nucleophiles via putative [(tpy)Ni-X] intermediates. Further mechanistic work, both experimental and computational, supported the involvement of these four-coordinate nickel halide intermediates in the cross-couplings. However, a detailed understanding of these paramagnetic species remained lacking. For this fiscal year, a synthesis has been developed that allows the isolation of four-coordinate [(tpy)Ni-Br] (1, tpy = terpyridine) in high yield. Complex 1 has been structurally characterized, and the X-ray data reveal a square-planar geometry, unlike the known [(tpy')Ni-I] (tpy' = 4,4',4''-tri-tert-butyl-terpyridine) but similar to [(tpy)Ni-CH_3]. In the solid-state, EPR spectroscopy indicates however, that unlike [(tpy)Ni CH_3], the electronic structure of 1 is a metal-centered, not a ligand-centered radical. DFT analyses support this assignment. The preparation of 1 also facilitated the analysis of the redox potentials of a series of terpyridine nickel derivatives. It was found that the overall ligand sphere (one versus two coordinated terpyridine ligands) plays more of a role in determining the redox potentials of these derivatives than do the formal oxidation states of the nickel ions in the solution phase. Details of this work have been published (Inorg. Chem. 2011, 50, 8630-8635).

The fluoroalkyl functional group confers special electronic properties to a molecule at both the local and global levels, and the development of new cross-coupling procedures will require a fundamental understanding of transition-metal fluoroalkyl complexes. With the explosion of interest in synthesizing organic molecules bearing perfluoroalkyl functional groups, we became interested in preparing complexes of late transition-metals that offer an internal spectroscopic handle to further study the electronic properties of perfluoroalkyl ligands. Since square planar nickel complexes of 2,2'-bipyridine (or derivatives) show intense metal-to-ligand charge transfer bands in the visible part of the electronic absorption spectra, we have decided to prepare three new complexes [(dtbpy)Ni(CF_3)2] (2), [(dtbpy)Ni(CF_2CF_3)2] (3), and [(dtbpy)Ni(CH_3)2] (4) (dtbpy = 4,4'-di(tert-butyl)-2,2'-bipyridine) to compare their absorption behavior. A detailed study of the UV-Vis spectra of the closely related complexes [(bpy)Ni(CH_3)2] (5), [(bpy)Ni(Mes)2] (6), and [(bpy)Ni(Mes)Br] (7) (Mes = mesityl = 2,4,6-trimethylphenyl) has recently been reported, and while the low energy transitions responsible for the long-wavelength absorption of 6 and 7 have distinct contributions from the aryl co-ligand, 5 exhibited almost pure metal(d)-to-ligand(p*) charge-transfer transitions. With this in mind, we were quite interested to see how the optical spectrum would change upon fluorination of the alkyl co-ligands, as changes would directly reflect the electronic properties of the metal and fluoroalkyl groups. We have been able to successfully prepare 2-4. The perfluoroalkyl complexes, unlike the nonfluorinated dialkyl derivatives are thermally quite stable, despite extremely distorted square-planar geometries. DFT analysis of both [(bpy)Ni(CF_3)2] and [(bpy)Ni(CH_3)2] predicts a large stabilization of the HOMO for the bis-CF_3 complex, which is consistent with the observed stability, oxidation potential, and optical spectrum relative to those for the bis-CH_3 complex. Our computational data also highlights the fact that, when comparing alkyl versus fluoroalkyl ligands, calculated atomic charges are most meaningfully discussed in combination with global molecular orbital energy considerations. This work has been submitted for publication.

Finally, inexpensive nickel-bipyridine complexes were found to be active for the trifluoromethylthiolation of aryl iodides and aryl bromides at room temperature using the convenient and inexpensive [NMe_4][SCF_3] reagent. This represents a significant advance from the state-of-the-art protocol, which uses an expensive and custom phosphine ligand, an expensive palladium salt, a quaternary amine additive, and stoichiometric use of an expensive silver SCF_3 derivative. Our nickel method could remarkably even trifluoromethylthiolate even aryl bromides at room temperature with good substrate scope. This work has been submitted for publication.

Chemistry of Complexes With Transition Metal-Heteroatom Bonds: Novel Insertion Chemistry and X-H Bond Activation

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Funding:	$175,000

Under support of DOE, we have sought to discover new elementary reactions with which one can build new catalytic processes. During the past several years, we have been studying the chemistry needed to develop aminations of olefins and catalytic transformations of amines. In particular, we have been conducting studies to understand the factors controlling migratory insertions of alkenes into metal-amide and –alkoxo bonds and the N-H oxidative additions of amines and ammonia equivalents to the system we showed previously to add ammonia.

Billions of pounds of polyolefins, carboxylic acids, and aldehydes are prepared annually from alkenes by homogeneous catalysis. A large fraction of these materials are ultimately converted to amines. Thus, much energy, waste, and capital construction cost would be reduced if amines and other nitrogen containing chemicals could be prepared directly from alkenes. Unfortunately, amines and ammonia are often poisons to transition metal catalysts, and the cleavage of the N-H bond of an amine is challenging under neutral catalytic conditions because N-H bonds are only weakly acidic, and the electron pair leads to formation of Lewis acid/base adducts that are more stable than the complexes generated from N-H bond cleavage. Thus, our studies to understand the organometallic chemistry of N-H bond cleavage and reactions of amido complexes with olefins should lead to an ability to form amines directly from alkenes without the need to generate alcohols, acids, and other oxygenated compounds as intermediates.

Cyanometallates, Their Cages, and Associated Host-Guest Behavior

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The project “Organometallic and Catalytic Chemistry of Functionalized Complexes” consists on three subprojects focused on applications of speciality 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 p-donation. The first project addresses fundamental questions associated with how electron-transfer influences reactions of homogeneous catalysts. We introduce a new redox-active ligands of the type $FcCH_2PR_2$ where Fc is a modified ferrocene. These ligands are less non-innocent and more easily installed than traditional non-innocent ligands. The second project, which grew from work in the previous contract period, explores the formation and reactivity of a diphosphine-dialkoxide platform derived from coupling of phosphine aldehydes. This study promises to deliver a sterically and electronically novel platform. The third project focuses on an acyl-pyridinol ligand for controlling reactivity of iron hydride. The effort exploits a new route to a close mimic of a cofactor in a biological hydride transfer catalyst and examines associated tautomeric equilibria.

Reactivity & Structural Dynamics of Supported Metal Nanoclusters using Electron Microscopy, In-Situ X-Ray Spectroscopy, Elec. Struc. Theories, & Molec

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This program of work is investigating the complex structural dynamics of heterogenous catalytic materials, exploring their nature at atomic resolution with integrated methods of theory and experimental investigation. We have established that complex electronic effects accompany the metal support interactions that are commonly used to stabilize nanoscale metallic clusters against aggregation. These effects give rise to complex forms of structural relaxation that are in turn further mediated by the structural and electronic features that attend adsorbate bonding. Our work is establishing these atomistic origins and providing state of the art tools for their characterization using combined state of the art methods of atomic resolution electron microscopy, coherent electron diffraction, synchrotron X-ray absorption spectroscopy, and theory.

Our work is establishing a structural picture for these systems that is surprisingly fluctional, dynamical structures that broadly explore variably strained bonding states that further evidence explicit perturbations originating from the atomic and electronic structures of the near support interface.

Synthesis and Exploratory Catalysis of 3D Metals: Group-Transfer, and Alkane Activation and Functionalization with Greenhouse Gases

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With support from DOE-BES low-coordinate vanadium(+2) complexes having the skeleton (nacnac)V(X) (nacnac$^-$ = $[ArNC(Me)]_2CH$, Ar = 2,6-$^iPr_2C_6H_3$, X$^-$ = amide, or alkoxide ligand) have been prepared in our group in multi-gram scales. Our goal is to utilize these systems as templates for small molecule activation, and then take advantage of the V(+3) <-> V(+5) redox couple to promote H-X bond activation (functionalization of the small molecule), and then promote product release. These highly reduced forms of low-coordinate vanadium are the first of their kind, and are thus highly reactive. They have given rise to dinitrogen complexes $[(nacnac)V(X)]_2(mu_2;eta^1,eta^1\text{-}N_2)$ (upon exposure to N_2 at 25 ^oC and 1 atm), P_4 activation to form (nacnac)V(X)(*cyclo*-P_3), terminal vanadium imides (from organic azides), oxides (from N_2O or other O-sources) and sulfides (from S_8), and many other vanadium(+4) complexes bearing cumulene groups. My research group has also developed a convergent synthetic approach to vanadium complexes bearing a terminal nitride ligand, namely complexes of the type (nacnac)V(N)(X). We also provide compelling evidence for how these terminal nitrides are formed, in part provided by a series of crossover and synthetic experiments. Incorporation of the nitride ligand involves an unprecedented bimolecular pathway whereby nitrogen loss is promoted by a Lewis acid. These systems undergo at least two intersystem crossing pathways to form the nitrides (change from two high-spin vanadium(+3) to two S =0 vanadium(+5) complexes). In addition, reactivity studies surrounding the terminal nitride ligand are reported and in progress (C-H bond activation, Si-H activation, carbonylation, reduction, etc), including catalytic S-atom transfer via a reactive thionitrosyl (nacnac)V(NS)(X) using elemental sulfur. Although the nitride motif has nucleophilic character, this one atom ligand serves as a conduit for electron transfer, thus promoting the reduction of the vanadium(+5) metal ion with concurrent oxidation of the incoming substrate.

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

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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.

Biomimetic Catalysts Responsive to Specific Chemical Signals

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Funding:	$440,000

One of the Grand Challenges in the new era of energy science is for scientists and engineers to “design and perfect atom- and energy-efficient syntheses of revolutionary new forms of matter with tailored properties.” Whether for structural formation, energy production, or enhanced properties, a material ultimately faces the issue of damage and need for replacement. A recent DOE report (Directing Matter and Energy: Five Challenges for Science and the Imagination) emphasizes some of the extraordinary processes that nature uses to address this issue (e.g., “the remarkable self-repair process of constantly manufacturing more of the catalytic component that ‘wears out’ and replacing it”). The report also highlights the importance of developing catalysts “capable not only of self-repair, but of self-correction in activity and selectivity in response to a changing reaction environment or a challenging substrate.” Unfortunately, although this type of “smart” catalysis is the norm in the biological world, its realization in synthetic systems is a difficult challenge.

The proposed research is based on inspirations from allosteric enzymes and the learning in oligocholate foldamers developed in the PI's laboratory. The preliminary data demonstrates the feasibility of creating oligocholates responsive to solvents/metal ions/small molecules and converting them to environmentally responsive catalysts. In this application, oligocholate foldamers with metal-binding ligands will be synthesized to catalyze industrially important reactions such as hydrogenation, hydroformylation, olefin epoxidation, and epoxide hydrolysis. The catalysts are designed to respond to solvent polarity, metal ions, and small molecules. The proposal illustrates general strategies to create (a) biomimetic allosteric catalysts, whose activity is tuned by their binding of a guest, and (b) induced-fit catalysts that change conformations upon interacting with appropriately functionalized substrates.

The research described in the proposal has important impacts on fundamental and applied energy-related sciences. On the fundamental level, it tests important biocatalytic principles on relatively simple synthetic systems and is expected to afford deeper understanding of biological catalysis. It represents an innovative combination of bio-inspired conformational control and synthetic organometallic catalysis. On the practical level, the research is anticipated to lead to "smart" catalysts and open up exiting applications in chemical analysis, reaction control, and materials synthesis. Signal amplification, for example, is possible if an analyte can turn on a catalyst and produce many copies of another detectable molecule. Advanced process control is possible if a catalytic reaction can be regulated by prescribed chemical or physical signals. Self-repair of a material is possible if a catalyst can detect material damage—by detecting either the physical stress or the molecules produced during structural damage—and produce new materials as a replacement or repair. Systems with feedback capabilities can be engineered if the product (i.e., "metabolite") of one reaction can regulate another reaction in predictable manners.

Engineering Catalytic Nanoporous Metals for Reactions Important to the Hydrogen Economy

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The development of new catalysts for hydrogen fuel cell reactions is a critical step in the development of this technology. Factors for which there is room for improvement include improving the catalyst activity, particularly toward oxygen reduction, and the development of carbon-free catalyst layers in the membrane electrode assembly that are not prone to corrosion. A materials system that may be a potential solution for both of these problems simultaneously are nanoporous metals made by selective electrochemical dissolution of one component of a multi-component alloy (dealloying). More specifically, alloys are chosen such that as the majority alloy component is dissolved, the secondary component diffuses along the alloy/electrolyte interface, reconstructing the material into a high surface area crystal with open porosity, high surface area/volume (ligament and pore sizes 5-10 nm), and intrinsic electrical contact to all surface area. In the last year, we have focused on the formation of core/shell nanoporous NiPt (np-NiPt) and related alloys. By impregnating the matrix np-NiPt of with a protic, hydrophobic ionic liquid that absorbs oxygen from the external environment, we have created a composite catalyst that geometrically confines oxygen in the catalytic region, potentially leading to orders-of-magnitude increases in that mass activity of the composite over nanoparticle-based catalysts.

Isotopic Studies of O-O Bond Formation During Water Oxidation

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Funding: $165,000

Since the last report, we have made significant progress in our experimental approach and theoretical understanding of O–O bond formation between metal-oxo complexes and water. It is widely held that this pivotal step controls the barrier to many "water-splitting" reactions: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$; where $4H^+ + 4e^- = 2H_2$. O–O bond formation is an intrinsically challenging process during photosynthetic water oxidation as well. It has been difficult to study and identify reactive intermediates generated within the oxygen-evolving complex of photosystem II (PSII). To illuminate the mechanisms of water oxidation in natural and synthetic systems and with an eye towards rational catalyst design, our efforts during the previous project period were dedicated to developing methods for measuring competitive oxygen-18 kinetic isotope effects (^{18}O KIEs) and making comparison to calculated transition states using Density Functional Theory. To this end, we have synthesized several inorganic complexes which mediate water oxidation and examined their catalytic reactions in the presence of sacrificial oxidants such as Ce^{IV} in strongly acidic media or $[Ru^{III}(bpy)_3]^{3+}$ photo-generated from $K_2S_2O_8$ in phosphate buffer near neutral pH.

As a complement to the isotopic measurements, our investigations have focused upon the steady-state kinetics of O_2 production at varying pH and Ce^{IV} concentration. Comparison of the kinetics to those of single-turnover reactions, can allow identification of the rate-limiting step(s). These kinetic data, together with electrochemical data, are useful in devising reaction coordinate diagrams within the construct of Marcus Theory. Specifically, the Marcus Cross Relation can successfully predict barriers to electron transfer and proton-coupled electron transfer reactions, which are key steps in all water oxidation reactions. We are testing proposed kinetic mechanisms by comparing measured ^{18}O KIEs to those predicted from the vibrational frequencies of intermediates and transition state structures. The following inorganic catalysts are being subject to these investigations: dimeric ruthenium complexes, monomeric ruthenium complexes, monomeric iridium complexes, tetranuclear cobalt polyoxometallate and cubane complexes, as well as a dimeric manganese complex that serves as a model for PSII. In addition, the stoichiometric oxidation of water by ferrate ($Fe^{VI}O_4^{2-}$) provides a case for relating measured ^{18}O KIEs to a series of computed transition states for O–O bond formation.

Isotope ratio mass spectrometry (IRMS) allows for the quantification of oxygen isotope fractionation, by comparing the $^{18}O/^{16}O$ content of O_2 produced to that of natural abundance H_2O. Using this method, we have determined competitive ^{18}O KIEs for the complexes above under various experimental conditions. In all cases, normal ^{18}O KIEs are observed which range from 1 to nearly 4 percent (1.010-1.040). These observations are in marked contrast to the negligible and inverse ^{18}O KIEs that have been associated with water oxidation by PSII in whole cells and chloroplasts. The unchecked reduction of O_2 produced from the water is a competing side-reaction in the multimeric PSII and obfuscates the observed ^{18}O KIEs. For this reason, the synthetic catalysts provide valuable benchmarks. Computational analyses predict that normal ^{18}O KIEs derive largely from the mass-dependence of the reaction coordinate frequency, (*i.e.* the imaginary mode for transition state decomposition). The contribution of this effect strongly indicates a mechanism involving some degree of rate-limiting O–O bond formation during catalytic turnover. In conclusion, the results obtained for an array of catalysts and stoichiometric oxidants hold promise for defining mechanisms of O–O coupling during water oxidation and calibrating the DFT computational methods intensively used in this area of sustainable energy research.

Nanoscale Molecules Under Thermodynamic Control: Digestive Ripening" or "Nanomachining""

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Funding:	$150,000

An important part of the work is in developing novel synthetic methods to metal and semiconductor nanoparticles, and post-synthesis manipulating these nanoparticles by chemical means to achieve high quality monodisperse particles. We have demonstrated that digestive ripening, a thermodynamic phenomenon where nanoparticles prefer certain sizes, is quite common, and has been observed for numerous materials, first in our laboratories, but now in many others around the world. For example, Cu, Ag, Au, Co, Pd, In, CdS, CdSe, CdTe, PbS, LiF, and other nanoparticles have been found to undergo digestive ripening.

Importantly, this process is dependent on the nanoparticle capping ligand (thiols, amines, carboxylic acids, phosphines), concentration of the ligand, concentration of capped nanoparticles, solvent employed (toluene, t-butyltoluene, butanone, water, etc.), time, and temperature. Thus, it is a “chemist’s playground,” and with important implications for many important technologies.

We have also discovered “reverse digestive ripening” where monodisperse particles can be destroyed by the addition of ionic surfactants and regenerated by removing these ionic surfactants and doing the digestive ripening again.

Very recent work has centered on fundamental studies of one material (gold) and comparing different ligands. This work has revealed why, in some cases, nanoparticles of about 3800 atoms and 350 ligands [$Au_{3800}(SR)_{350}$] are formed, but in other cases, very small clusters are formed, such as $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, or $Au_{144}(SR)_{60}$. A key finding is that certain thiols can oxidize Au^{o} to Au^{+} and form a $(AuSR)_n$ polymer. Treatment of this polymer, with a strong reducing agent, leads to small gold clusters, whereas, if the $(Au\text{-}SR)_n$ polymer formation can be avoided, the larger Au_{3800} nanoparticles are formed preferentially.

Other ongoing work deals with trying to understand what size range of metal nanoparticles are susceptible to digestive ripening, and what ligands interact in a bond breaking way; for example, we have recently shown that the following reaction takes place at low temperature with small “naked” gold nanoparticles: $(Au)_x + HS\text{-}R \rightarrow (Au)_{x-1}AuS\text{-}R + \frac{1}{2}H_2$

Regarding size of nanoparticles that are susceptible, we have found that 40 nm particles will react if they are polycrystalline. These are broken down eventually forming 4-6 nm species with surface bound thiolates. Smaller particles are more susceptible to further reaction, and the small metal cluster-thiolate structures can form. The size of the nanoparticles is crucial; larger nanocrystals will react, but only on the surface, while very small ones are more reactive and can be further “consumed.”

Fundamental Surface Structure-Photoactivity Relationships of Semiconductor Mixed Oxides for Splitting of H_2O to H_2/O_2

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The development of photocatalytic conversion of cheap and abundant H_2O to clean, non-carbon H_2 fuel is one of the most important technological challenges of the 21st century. The objectives of this research proposal are to (1) establish the fundamental surface structure-photoactivity relationships for H_2O splitting to H_2 fuel that will enable rational design of novel semiconductor-based photocatalytic inorganic oxide materials and (2) advance the development of time-resolved spectroscopic techniques that can provide surface information in various environments. The research will focus on both model supported oxide molecular structures and advanced photocatalytic bulk mixed oxides. The supported surface oxides will be synthesized by self-assembly, and the advanced bulk mixed oxide photocatalysts will be obtained from the leading photocatalysis laboratory of K. Domen (Tokyo University). The molecular and electronic structures of the photocatalytic supported multicenters and the reaction intermediates under different conditions will be determined with in situ/operando optical spectroscopic characterization methods (visible and UV Raman, IR, UV-vis, photoluminescence (PL) and time-resolved picosecond PL-Raman). The nature of the outermost surface layers of modified and unmodified bulk mixed oxide photocatalysts will also be characterized with Lehigh's unique multiple, cutting edge surface characterization instruments [high-resolution x-ray photoelectron spectroscopy (HR-XPS) and high-sensitivity low energy ion scattering (HS-LEIS)]. The model supported oxide molecular multicenters will be examined for their photocatalytic efficient splitting of water to H_2/O_2, which, when combined with the optical characterization information, will allow for the establishment of fundamental structure-photoactivity relationships. The model supported oxide systems will provide fundamental insights on how photoactive surface sites can be modified by secondary oxides as well as provide structure-photoactivity information. These insights will be extended to surface modification of the advanced bulk mixed oxide photocatalysts for enhanced photoactivity.

Catalysts for Energy-Efficient Dinitrogen Activation and N-Atom Transfer Processes

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The significance of the project is that the current energy and environmental costs for existing nitrogen-based fertilizer production employing the Haber-Bosch (HB) process, which converts dinitrogen to ammonia through direct hydrogenation over iron-based catalysts at high temperature and pressure, are quite high. More specifically, based on present technology, ~33,000 cubic feet of natural gas is required to provide both the energy and the source of hydrogen to produce one ton of nitrogen-based fertilizer employing the HB process.

The central hypothesis of the project is that the unique steric and electronic features of the monocyclopentadienyl (η^5-C_5R_5), amidinate {κ^2-[N(R^1)C(R^2)N(R^3)]} (CpAm), and guanidinate {κ^2-[N(R^1)C{N(R^2)$_2$}N(R^3)]} (CpGu) ligand environments are ideally suited for experimentally and computationally investigating group 4 – 6 early transition metal-mediated N_2 activation, N-N bond cleavage, and N-atom functionalization within several LCIS series of CpAm- and CpGu-based $[L_nM]_2(\mu\text{-}N_2)$ 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.

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 multiple bond activation and cleavage, including the molecular and electronic structures of ground-state precursors, intermediates, and products, together with 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 N_2 activation, N-N bond cleavage, N-atom functionalization, and N-atom transfer processes.

The intellectual merit of the project is realization that the specific aims of the project should aid the development of more energy-efficient “cleaner” technologies that can be used in support of the Haber-Bosch process for ammonia-based fertilizer production, possible alternatives to the Haber-Bosch process itself, and ultimately, to other more energy-efficient catalytic processes that can serve to reduce environmental penalties associated with the Haber-Bosch process in terms of a reduction in associated CO and CO_2 carbon loads.

The broader impact of this work will be the potential development of more efficient catalysts for direct N_2-reduction and N-atom transfer processes that will be beneficial to both the world economy and society. The proposed work will further provide an important vehicle by which future generations of undergraduates, graduate students, and postdoctoral researchers can be trained. The ability to achieve success in the latter objective rests on the strong documented track record that the University of Maryland has achieved in the recruitment, retention, and graduation of individuals from underrepresented groups.

The Living Polymerization of 1,6-Heptadiynes

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A major application of well-defined metathesis catalysts is ring-opening metathesis polymerization (ROMP). This type of metathesis catalyst is fundamentally new in a way that is likely to be of major importance to ROMP chemistry. These catalysts control polymer structure through stereogenic metal (SM) control, which is now possible because the metal is chiral and inverts with each polymerization step. We plan to expand the design of catalysts in order to allow us to prepare all four major polymeric

ROMP structures derived from a wide variety of norbornadienes or norbornenes. Since polymer properties are dictated by polymer structure, we predict that precise control of polymer structure will have major implications in the design of specialty polymers for a wide variety of applications (in which atactic ROMP polymers have been employed) that have emerged in the last decade.

Adsorbate-Adsorbate Interactions on Metal Surface: First Principles DFT and ab-initio Thermodynamics Studies of Alkali Promotion in Heterogeneous Cata

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GOALS

Develop physically transparent, predictive models relating the perturbations of metallic surfaces, by chemical promotion (for example promotion by alkali adsorbates), poisoning, or alloying, and the chemical and catalytic behavior of those surfaces.

DOE INTEREST

Identical surface sites of neighboring metals in the periodic table of elements bind various adsorbates by up to ~ 1 eV (~ 100 KJ/mol) difference in adsorption energies, which means that while one metal might be chemically inert for a particular chemical transformation, its first neighbor in the periodic table might be overly chemically active (it gets poisoned by adsorbates) and equally catalytically inefficient. Obviously, the optimal material would be somewhere in between these two extremes. Rapid identification of optimal metal catalysts (for example, alloys or promoted metals) has been hampered by the lack of predictive models that would guide us in the discovery of these catalysts. For example, reliable models to predict how the adsorption energy of an adsorbate on a metal surface changes as the local chemical environment of the adsorption site is changed by the formation of an alloy or intermetallic compound are lacking. The lack of these models, along with the immense size of the phase space of available promoter, poisons, and alloys, makes it almost impossible to identify optimal catalytic materials. The central question we attempt to answer in this project is the following: how does a perturbation of a metal surface (by promotion, poisoning, alloying) affect the chemical activity of the surface? The ultimate objective is to develop simple predictive theories that can guide us in the discovery of novel, more efficient multi-component catalysts. This objective is critical for accomplishing a long-term DOE goal of “heterogeneous catalysis by design.”

RECENT PROGRESS AND MAIN ACCOMPLISHMENTS

(1) We have developed a very general and physically transparent model, based on DFT methodology, which allows us to identify underlying physical mechanisms that govern the changes in the chemical activity of a metal surface as this surface is perturbed. This framework can be used to study various perturbations, including chemical promotion and alloying.

(2) This model was utilized to examine the effect of Cs adsorbates (promoters) on the O_2 dissociation reaction on Ag(111). These studies revealed that the main mode by which Cs affects the dissociation of

O_2 on Ag(111) is a long-range electrostatic/polarization interaction between Cs and relevant reaction intermediates. These interactions stabilize the transition state involved in the dissociation of O_2, therefore lowering the activation barrier. It was shown that these conclusions in general apply for any combination of electronegative adsorbates and electropositive promoters on metal surfaces.

(3) We have also studied how a working state of an alkali promoter changes as a function of external conditions, i.e., pressure and temperature of reactants. In this context, we have examined possible formation of Cs-oxide complexes as a function of the chemical potential of gas-phase O_2 (pressure and temperature). We employed ab-initio statistical mechanics and ab initio kinetic Monte Carlo simulations to show that finite temperature and pressure of reactants can significantly affect the mechanism and extent of alkali promotion.

(4) We have studied the effect of alkali promoters on the working state of promoted metal surface. The studies showed that alkali promotes can affect not only the kinetic of surface reactions but also the working state of the promoted catalytic material by affecting the on- and sub-surface steady state concentration of adsorbates. More specifically, we found that Cs affects the uptake of oxygen by Ag (and therefore change in the oxidation state of Ag).

(5) We have also employed the model, developed under Accomplishment 1, to analyze mechanisms associated with the changes in the chemical activity of metal surfaces in response to the formation of alloys. In this context, we developed a predictive framework that can relate the geometric structure of an alloy to its chemical activity using only measurable physical characteristics of the constitutive metals in their pure unalloyed form. This framework opens up avenues for a very rapid screening for optimal alloys for various chemical transformations.

(6) We performed a number of experimental studies verifying and validating the predictive capacity of the proposed framework.

(7) The model was used to screen for novel Pt-based catalyst for the electrochemical oxygen reduction reaction (ORR). The model achieved many promising alloy compositions that perform the ORR reaction with lower over-potential losses than pure Pt. Some of the predictions were validated experimentally. The model was also used to outline general strategies for the synthesis of optimal ORR electro-catalysts.

(8) The model was also use to identify Ni-based alloy catalysts that show improved resistance to carbon-induced deactivation compared to pure Ni.

Catalytic Oxidative Coupling of Arenes and Alkanes: Applications for Efficient Chemical Synthesis and for Hydrocarbon Oligomerization

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Funding:	$130,000

The overall research goals and specific objectives for this project are to (1) conduct a detailed mechanistic study of a novel Pd-catalyzed, benzoquinone promoted arene oxidative cross-coupling reaction; (2) use the mechanistic insights elucidated in these studies to control selectivity in Pd-catalyzed arene oxidative coupling reactions; (3) assay Pt and Pd-based catalysts for selective non-directed arene activation; and (4) study applications to C–H oxidative coupling and other C–H functionalization reactions. We anticipate that these studies will be applicable to developing a variety of new Pd- and Pt-catalyzed oxidative coupling transformations. This research provides an atom efficient and environmentally benign alternative route to the synthesis biaryl compounds, which are critical structures in a wide array of pharmaceuticals and fine chemicals. In addition, similar catalytic strategies can ultimately be applied for the oxidative oligomerization of alkanes, providing a direct and energy efficient route from natural gas to liquid fuels and providing an attractive approach to upgrade low molecular weight by-products of the Fisher Tropsch.

Bio-inspired Iron Catalysts for Hydrocarbon Oxidations

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The oxidation of hydrocarbons is a process of both biological and industrial importance. The goals of this project are to develop iron catalysts for hydrocarbon oxidations and to understand their mechanisms of action. The design of these iron catalysts has been inspired by the many nonheme iron oxygenases that nature has evolved to carry out the stereoselective oxidation of C-H and C=C bonds. Of particular interest are the Rieske dioxygenases, which utilize a mononuclear $Fe(His)_2$(carboxylate) active site to catalyze the cis-dihydroxylation of arene double bonds, the only enzymes that effect this unique transformation. In the course of our DOE-supported project, we have identified the first examples of bio-inspired nonheme iron complexes that catalyze the room temperature cis-dihydroxylation of olefins and arenes using H_2O_2 as an economical, atom-efficient, and environmentally friendly oxidant. These reactions have the potential to serve as an alternative to chemical processes that rely on scarce and toxic heavy metals (e.g., Os). These catalysts can also carry out alkane hydroxylation and olefin epoxidation with high stereoselectivity. Two types of catalysts have been found. Class A catalysts generate an electrophilic oxidant that is proposed to have an $Fe^{V}{=}O$ unit, while Class B catalysts show an unusual preference for oxidizing electron-deficient olefins and are postulated to generate a nucleophilic $Fe^{IV}(OH)_2$ oxidant. The main goals for this proposed funding period are to obtain spectroscopic evidence for the respective $Fe^{V}{=}O$ and $Fe^{IV}(OH)_2$ oxidants proposed in Class A and B catalysis and understand their properties, carry out detailed kinetic studies on Class B catalysts to gain insight into their reaction mechanism and the accelerating effects of various additives, and develop more robust iron cis-dihydroxylation catalysts.

Polynuclear Aromatic Hydrocarbons with Curved Surfaces: Buckybowls

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Funding: $135,000

This program deals with the synthesis, structural studies, and chemistry of curved-surface, polynuclear aromatic hydrocarbons (PAHs) with carbon frameworks structurally related to fullerenes. They are referred to as “buckybowls” or “fullerene fragments.” Previous work under this DOE sponsored program produced several new buckybowls and, more importantly, resulted in a development of efficient, gram-scale solution synthetic methodologies for preparation of small buckybowls, most notably corannulene ($C_{2}0H_{10}$) and its derivatives.

During this funding cycle we plan to employ the corannulene-based synthons previously developed in our laboratory to prepare a number of highly nonplanar molecular architectures with two or more corannulene subunits. This “bottom-up” approach will produce well defined carbon-rich systems of nanometric scale which, besides their “pure chemistry” value will have a potential for applications as novel materials in separation sciences, nanoelectronics, photovoltaics and catalysis.

We have two broader objectives for the cycle, as listed below:

(1) Synthesis of Bowl Shaped Systems of Nanometric Dimensions. Utilizing the palladium-catalyzed cyclotrimerization reaction of 1,2-didehydrocorannulene and Diels-Alder cycloaddition methodology we will prepare a number of large, highly nonplanar systems with multiple corannulene subunits. In combination with cyclodehydrogenation chemistry this approach will produce carbon-rich discotic bowls of nanometric size with a potential for self-assembly and liquid crystal formation.

(2) Molecular Receptors with Corannulene Pincers. As we showed recently “molecular clips” with corannulene pincers can act as molecular receptors for fullerenes, binding through $\pi-\pi$ convex-concave stacking of the curved conjugated carbon networks. We propose a preparation and testing of a number of new molecular receptors with two or more corannulene clips with improved affinity and specificity toward guest molecules, including fullerenes. Tuning of the hosting properties will be achieved by engineering the topology of the tethers. An integrated approach to the design of efficient clips, which combines computational screening of potential receptors followed by synthesis of the best candidates and experimental testing of their complexation abilities will lead to molecular receptors for fullerenes which are even more efficient than “buckycatcher,” prepared recently in our laboratory.

The proposed research focuses primarily on synthetic methodologies leading to buckybowls. However, since we can produce sufficient amounts of these hydrocarbons, we will also be able to explore their properties and potential applications. We hope that this novel class of materials will soon fulfill some of the promises for their applications in science and technology.

Platinum Oxo Complex Reactivity and Dioxygen Activation

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Funding:	$150,000

OVERALL RESEARCH GOALS

- Understand factors in late transition metal oxo and hydroxo complex reactions with alkenes and other unsaturated substrates.
- Develop molecular oxygen chemistry of late transition metal complexes as a platform for the reduction of molecular oxygen to oxo complexes.
- Understand and control halogen photoelimination reactions from late transition metal complexes as part of a cycle to store solar energy.

SPECIFIC OBJECTIVES

- Delineate the reaction mechanism of simple alkenes with electrophilic Pt(II) hydroxo complexes.
- Confirm the role of steric interaction in photohalogen eliminations in Pt(IV) organometallic complexes.

SIGNIFICANT ACHIEVEMENTS AND RESULTS FOR THE YEAR

- Elucidated the ethylene reaction pathway for a highly reactive platinum hydroxo complex.
- Observed an unusual trend in substituted alkenes of potential relevance to alkene oxidation.
- Discovered an apparent steric effect that promotes bromine photoelimination from a highly tunable Pt(IV) organometallic complex.

POTENTIAL IMPACT IN SCIENCE AND IN TECHNOLOGIES OF INTEREST TO DOE

- Improve our understanding of the chemistry of late transition metal dioxygen, oxo, and hydroxo complexes. This chemistry is fundamental to critical steps in many catalytic processes involving oxygen species important in many area of interest to DOE including fossil fuel conversion into industrial and consumer chemicals, energy conversion involving both fossil fuels and renewable fuels, and in pollution control processes. Understanding the chemistry will lead to benefits that include increased process efficiency, new and better processes for chemical and energy conversion, and less pollution.
- Halogen photoelimination studies are relevant to the conversion and storage of solar energy. Our results could be applied not just to halogen eliminations but also to other photochemical reactions leading to efficient systems for solar energy processes.

Mechanisms of N-H Bond Formation Relevant to Nitrogen Fixation

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The chemistry of high valent iron nitrides supported by bulky tris(carbene)borate ligands has been investigated. Following an earlier report of nitrogen atom transfer from an iron(IV) nitride complex to triphenylphosphine, a combined experimental and theoretical investigation into this reaction was undertaken. A key result of this study is the discovery of a dual nature transition state for atom transfer in which there are interactions between the nitrido HOMO and the phosphine LUMO, in addition to the expected HOMO-phosphine LUMO interaction. Interestingly, the iron(II) phosphoraniminato complexes undergo a thermal spin crossover process, the first such observation for a four-coordinate iron(II) complex. Nitrogen atom transfer from the iron(IV) nitrides to a number of hydrocarbon substrates occurs, including alkenes, resulting in the formation of iron(II) aziridino complexes. Complete nitrogen atom transfer to substrates is observed in some cases. Oxidation of an iron(IV) nitride complex allows for the first crystallographic characterization of an iron(V) complex, which has also been characterized by Mössbauer, EPR, ENDOR and resonance Raman spectroscopies. This complex is highly reactive, and produces quantitative ammonia from water and a suitable electron source.

Direct Partial Oxidations Using Molecular Oxygen

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Funding:	$250,000

Our team has been investigating a possible catalytic cycle with the goal of developing catalysts for the partial oxidation of alkenes using molecular oxygen as the oxidant. There are three steps in the cycle: (1) hydrogenolysis of a M-OH bond to afford a M-H and water, (2) insertion of O_2 into the M-H bond to form a reactive M-OOH species, and finally (3) transfer of oxygen to the olefin by MOOH, regenerating M-OH.

This past year, extensive studies on step 1 have provided key insight into the mechanism and scope of hydrogenolysis of the M-OR linkage. A series of pincer (tBuPCP)PdOR complexes (tBuPCP = 2,6-bis(CH_2PtBu_2)C_6H_3, R = H, CH_3, C_6H_5, $CH_2C(CH_3)3$, CH_2CH_2F, CH_2CHF_2, CH_2CF_3) and their reactivity with hydrogen was investigated. Whether hydrogenolysis, ß-hydride abstraction, hydrolysis (by adventitious water), or even a lack of reaction was observed was found to be controlled by the basicity of the –OR group, its steric bulk, and its susceptibility to a dissociative ß-hydride abstraction pathway. This work will broadly inform the field as to the varied reactivity of M-OR linkages and in how to control selectivity.

In the investigation of step 2, we have further examined various pincer ligand-palladium combinations via DFT calculations and have shown that all appear to proceed by the direct attack on the Pd-H by oxygen, with varying barriers for insertion.

We have also made progress during the last year on our efforts to promote the challenging oxygen atom transfer of Step 3. We have shown via DFT calculations that this O-transfer step is energetically favorable overall, although it is proving to be difficult experimentally. Two promising strategies for this transfer have been identified and our investigations of these methods are ongoing. One strategy involves a tandem catalytic approach, using a second metal center to bind the olefin, thereby increasing the susceptibility of the olefin toward reaction with the MOOH complex. Several olefin complexes have been designed and prepared toward this end. Studies of their reactions with the PCPPdOOH and other oxygen transfer reagents are in progress. The other strategy requires an ambifunctional ligand on the M-OOH complex. The ligand is proposed to assist in the proton transfer between the ß and a oxygen of the OOH linkage lowering the transition state energy for ß oxygen transfer to the olefin. A variety of specific ligand structures have been identified and synthetic routes are being developed. A third strategy involving a hemilabile PCO ligand to allow coordination of the olefin to a PdOOH center has been reconsidered due to an unexpected competing reductive elimination. Nevertheless, the variety of complexes with different ligand coordinations prepared and characterized in this study provides considerable insight to the use of hemilabile ligands in catalysis.

Lastly, in step-out work, we have continued research on an alternative route using a Cu-based heterogeneous catalytic system. In this system we have produced various oxidized products, including epoxides, and work continues to understand the optimal experimental conditions to maximize yields of the desired products, as well as understanding the interactions between Cu and the supports used.

Nanostructured Catalysts for Hydrogen Generation from Renewable Feedstocks

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Funding: $225,000

The objective of the proposed research is to gain a 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 will synthesize catalysts that are well-defined: single phase, uniform composition metallic alloy powders. We will also synthesize oxides of controlled morphology that expose well-defined single facets so that the role of the oxide phase can be studied. These catalysts will be studied using novel analytical approaches including the use of in-situ microscopy and spectroscopy techniques. The research program will be comprehensive in nature and will include 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. The methods developed in this work will be applied to the Ethanol Steam Reforming (ESR) as a test reaction. ESR was selected because it is a natural extension of our previous studies of methanol steam reforming, but provides additional complexity and represents a bio-renewable feedstock.

The proposed research will result in the development of methodology for the study of complex multi-metallic catalysts. For example, the metal alloy nanoparticles allow definitive measurements of the specific reactivity of the metal phase in supported metal catalysts, in a manner similar to that achieved via single crystals in ultra high vacuum surface science studies. The results will provide the scientific basis needed for the control of C-C, C-O, C-H, O-H bond cleavage which is not only important in development of highly active and selective catalysts for the production of H_2 via the steam reforming of alcohols, but also for the control of chemical transformations in biomass-derived-feedstocks. This project will expand the toolkit for the study of catalysts through advanced characterization techniques so that new catalytic materials can be developed based on the fundamental knowledge that is obtained. Novel catalytic materials, in the form of atomically dispersed transition metals, and controlled facet oxides, will also be developed.

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

As part of our long-term goal of developing methodologies for the conversion of poly-saccharide feedstocks (e.g., starch, cellulose, sugars) into value added materials, we have been investigating methods for activating the key anomeric linkage in sugars. This bond not only links the sugars together but is characterized by unique reactivity that results from enforced stereoelectronic effects. Learning to catalytically activate bonds at this center will provide the fundamental reactivity profiles that will eventually enable us to rationally design catalysts. Currently, we are investigating the fundamental reactivity of carbohydrates towards transition metal complexes. As oxygen-based leaving groups seldom undergo reactions that proceed through radical intermediates, we searched for a two-electron pathway that would enable glycosyl-electrophile activation. We found that the invertive oxidative addition of acetobromo-a-D-glucose to $Pd(PEt_3)3$ gives the air-stable ß-anomer of $Pd(PEt_3)2(Br)(AcO\text{-}glu)$, which represents the first crystal structure of a pyranosyl palladium complex. The compound undergoes slow ß-acetoxy elimination in solution to form tri-O-acetyl glucal and $Pd(PEt_3)2(Br)(OAc)$. In an effort to prevent this undesired elimination, we have recently begun to explore coordinatively saturated metal centers. Preliminary results show that CpMo(CO)3(BnO-glu) results from the oxidative addition of benzylbromo-a-D-glucose to the very nucleophilic CpMo(CO)3-. Future work will focus on developing these systems for carbohydrate functionalization. Additional efforts have focused on alternative methods of radical generation via photoredox catalysis. The applicability of our previously developed methods has been demonstrated through a practical large-scale synthesis of a key intermediate using a photoflow reactor and elaboration to amino acid derivatives.

Surface Chemistry Characterization of Novel Model Systems for Hydrodesulfurization Catalysis

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Funding:	\$120,000

This project consisted of two main project lines. First, characterization of novel nanomaterials for hydrodesulfurization (HDS) applications. Second, studying more traditional model systems for HDS such as vapor-deposited silica-supported Mo and MoSx clusters.

In the first subproject, we studied WS_2 and MoS_2 fullerene-like nanoparticles as well as WS_2 nanotubes. Thiophene (C_4H_4S) was used as the probe molecule. Interestingly, metallic and sulfur-like adsorption sites could be identified on the silica-supported fullerene-particles system. Similar structures are seen for the traditional system (vapor-deposited clusters). Thus, this may be a kinetics fingerprint feature of modern HDS model systems. In addition, kinetics data allowed characterization of the different adsorption sites for thiophene on and inside WS_2 nanotube bundles. The latter is a unique feature of nanotubes that has not been reported before for any inorganic nanotube system; however, examples are known for carbon nanotubes, including prior work of the PI. Although HDS has been studied for decades, utilizing nanotubes as nanosized HDS reactors has never been tried before, as far as we know. This is of interest from a fundamental perspective. Unfortunately, the HDS activity of the nanocatalysts at ultra-high vacuum (UHV) conditions was close to the detection limit of our techniques. Therefore, we propose to run experiments at ambient pressure on related nanopowder samples as part of the renewal application utilizing a now-available GC (gas chromatograph) setup. In addition, Ni and Co doped nanocatalyts are proposed for study. These dopants will boost the catalytic activity. First experiments at ambient pressure show that the novel doped nano-HDS catalysts are indeed catalytically active.

In the second subproject of the prior grant, we studied HDS-related chemistry on more traditional supported cluster catalysts. Mo clusters supported by physical vapor deposition (PVD) on silica have been characterized. Two reaction pathways are evident when adsorbing thiophene on Mo and MoS_x clusters: molecular adsorption and dissociation. PVD Mo clusters turned out to be very reactive toward thiophene bond activation. Sulfur and carbon residuals form, which poison the catalyst and sulfide the Mo clusters. Sulfided silica-supported MoS_x samples are not reactive toward thiophene bond activation. In addition to S and C deposits, H_2, H_2S, and small organic molecules were detected in the gas phase. Catalyst reactivation procedures, including O_2 and atomic hydrogen treatments, have been tested. Cluster size effects have been seen: thiophene adsorbs molecularly with larger binding energies on smaller clusters. However, larger clusters have smaller activation energy for C_4H_4S bond activation than smaller clusters. The latter is consistent with early catalysis studies. Kinetics and dynamics parameters have been determined quantitatively.

We spent a significant amount of time on upgrades of our equipment. A 2nd-hand refurbished X-ray photoelectron spectrometer (XPS) has been integrated into the existing molecular beam scattering system and is already operational (supported by the DOE supplemental grant available in October 2009). We also added a time of flight (TOF) system to the beam scattering apparatus and improved on the accessible impact energy range (new nozzle heater and gas mixing manifold) for the beam scattering experiments. In addition, a GC-based powder atmospheric flow reactor for studies on powder samples is now operational. Furthermore, a 2nd UHV kinetics system has been upgraded as well.

In summary, mostly single crystal systems have so far been considered in basic science studies about HDS. Industrial catalysts, however, can be better approximated with the supported cluster systems that we studied in this project. Furthermore, an entirely new class of HDS systems, namely fullerene-like particles and inorganic nanotubes, has been included. Studying new materials and systems has the potential to impact science and technology. The systems investigated are closely related to energy and environmental-related surface science/catalysis.

This prior project, conducted at NDSU by a small team (typically one postdoctoral fellow and one graduate student at a given time), resulted in a total of 19 printed publications. In addition, collaborators at national laboratories and abroad were part of the projects, as proposed. More specifically, projects about HDS on MoS_2 and WS_2 inorganic fullerene-like nanoparticles, inorganic WS_2 nanotubes, Mo and MoS_2 vapor-deposited nanoclusters, modeling, reviews/book chapter, and side projects have been conducted, as proposed, acknowledging funding from this grant.

Modeling of Catalytic Processes for More Efficient Utilization of Hydrocarbon Resources

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DOE-BES funded research from the past grant period provides a firm foundation for the current proposal. Continued integration of our modeling with work from leading experimentalists provides analyses of important catalysts that are more powerful than either theory or experiment in isolation. This integration can lead to quicker, more comprehensive solutions to DOE-BES technical challenges. Training early career scientists to succeed in multi-disciplinary research is another important benefit of our research program. Scientific areas targeted in this proposal include novel catalysts for olefin hydroarylation and nickel (Ni) complexes for catalytic group transfer to hydrocarbons.

With respect to hydroarylation catalysis, we will fully characterize reaction coordinates – main path and side reactions – for non-octahedral, non-d6 catalysts. Initial efforts will focus on promising, square planar d8-PtII catalysts recently disclosed by long-time collaborator and fellow DOE-BES contractee, Professor T. Brent Gunnoe (UVa). The role of metal, supporting ligation and activating ligand upon the activity and selectivity of said catalysts will be elucidated to assess the performance envelope of such catalysts and to provide guidance for experimental efforts. Modern computational chemistry will identify novel, experimentally plausible modifications to current generation PtII olefin hydroarylation catalysts that enhance activity and selectivity, in particular, catalysts that ameliorate undesired multiple alkylation.

For the nickel catalysis, we have formed strategic collaborations with two of the leading experimental groups in the area: Professors Tim Warren (Georgetown U.) and Greg Hillhouse (U. Chicago). The catalytic cycle for promising NiII systems for hydrocarbon amination and oxidation will be elucidated using modern computational chemistry methods. In conjunction with experimental collaborators, modifications to first generation systems will be sought in order to increase activity, selectivity and, especially, substrate scope. The study of nickel-imides will be extended to their oxo congeners, incorporating both surface and molecular models, to identify novel hydrocarbon oxidation catalysts.

While the hydroarylation research focuses on benzene and ethylene as substrates, relevant to bulk chemical synthesis, hydroarylation is also relevant to fine chemical synthesis. Moreover, C-H activation (the rate determining step) by transition metal complexes, and the related issue of metal-mediated H_2 activation, are important in many aspects of catalysis in the energy sector. Finally, late transition metal catalysis has undergone a tremendous renaissance over the past few years, in part due to the chemical flexibility we alluded to above. Hence, research towards understanding the performance envelope of such complexes and catalysts can help inform other research endeavors.

Understanding critical similarities and differences between precious and base metal catalysts is critical for engineering cheaper catalysts, and can aid in developing better precious metal catalysts. The same is true upon comparing traditional hydrocarbyl supporting ligands and Teflonized variants. Finally, extending promising chemistry from C-N to C-O bond formation would open new vistas late catalyst development. Finally, we can integrate the research on surface-supported Ni=O models with other research in our group on C-H activation by NiO(100), plus our planned modeling of molecular Ni-oxo models, to build in critical links between homogeneous and heterogeneous catalysis.

Transition metal chemistry plays a central role in the energy sector. In all technological applications, chemists seek to leverage the ability of transition metals to stabilize a diverse array of chemical states through modification of metal, ligand and substituents. In this regard, computational chemistry has played an increasingly important role, as an adjunct to experiment, in establishing structure-property relationships essential to rational design of new materials. Research aimed at understanding how one may fine- and coarse-tune chemical and physical properties of transition metal complexes thus significantly impacts the Catalysis Sciences program, specifically, but also the larger DOE-BES research portfolio.

Institute for Catalysis in Energy Processes

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Funding:	$1,000,000

The Institute for Catalysis in Energy Processes (ICEP) is a joint venture of the Northwestern University Center for Catalysis and Surface Science (NU) and Argonne National Laboratory (ANL). It is organized into three highly integrated efforts. Two of these comprise the scientific themes: chemical catalysis, selective oxidation of light alkanes to fuels and photocatalysis, and 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.

Molecular Nanocages for Catalysis: An Investigation of Effect of Active Site Environment

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Funding:	$170,000

Achieving high product selectivity in a chemical reaction would eliminate undesirable byproducts, reduce environmental impact of the process, and lower the energy consumed for separation and purification, which often accounts for the majority of the process energy requirement. The objective of this research of this project is to acquire knowledge, develop insight, and incorporate enzymatic functions into nonbiological structures, with the goal to (1) identify important bonding and nonbonding interactions that render enzymes their activities and selectivities, so as to design nonbiological catalytic structures to capture these properties, and (2) develop synthetic techniques and acquire know-how to synthesize the desired structures.

Our strategy is to design and synthesize molecular-size structures based on siloxane and carbosilane that are versatile and amenable to the introduction of different functional groups at specific locations. Siloxane and carbosilanes are attractive because of the flexible O–Si–O and C–Si–C bond angles that make them susceptible to conformational changes in response to specific interaction with reactant molecules (the induced-fit phenomenon). A major focus of our work at this stage is to develop the know-how to synthesize multifunctional ligands for metal complex catalysts.

Our previous experience suggested that acyloxysilyl bonds may be quite useful for our synthesis of designed catalytic structures. However, its high reactivity may severely limit its application. In order to determine it usefulness to our work, we examined the properties of these bonds, R3Si-O-(C=O)-R, also known as silyl ester bonds, for conditions that could be useful for our synthesis of degradable templates and precursors for carboxylate groups in a structure. One potential complication with molecules containing these bonds is the exchange of the ester ligand with chloro ligands. Thus, the exchange of chlorosilyl groups in a series of dichlorosilanes with acyloxysilyl groups was measured. We found that the exchange reaction depends strongly on the nature of the remaining silane ligands. Thus, it is possible to identify a set of reaction conditions under which silyl esters can be used in synthesis without significant side reactions.

Separately, we extended our earlier work that showed that the stability of a Pd acetate catalyst in aerobic oxidation of phenol and the reaction kinetics depend strongly on the length of the bispyridylsiloxane ligand of the Pd ion. The effect of a third functional group on these bispyridyl lignads was examined. We hypothesized that interaction of the third functional group either with the Pd center or with the reaction substrate would result in changes in the reaction pathway, which would be manifested in a change in reaction selectivity. Bispyridyl ligands containing carboxylate as the third functional group were synthesized. They were found to bind to the Pd center much more strongly than bispyridyl ligands without the third group. We are beginning to examine the effect of these ligands on Pd catalyzed reactions.

Our future plan is to further extend the concept of utilizing non-covalent bonding interactions to effect changes in reaction selectivity. In order to minimize the chance of formation of multinuclear macrocycles with multifunctional ligands, we plan to immobilize them (and thus the catalyst) on a support surface, such as silica. In this way, we will generate a single site catalyst. Furthermore, our synthesis scheme will be designed to permit controlling the distance between the hydrogen bond acceptor/donor groups and the metal center, thus allowing for selective binding of the substrate. It will be interesting to examine the effect of the silica surface with respect to restricting the free rotation of the siloxane tether connecting the metal and the hydrogen bond acceptor/donor groups.

Raman Spectroscopy of Working Catalysts

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Resonance Raman spectroscopy is capable of detecting catalytic reaction intermediates, carbonaceous deposits (coke) responsible for catalyst deactivation, and the molecular nature of catalytic oxide layers. The high sensitivity of UV Raman spectroscopy, due to the minimization of fluorescence, also makes it possible to study catalysts with exceedingly low loadings of the active oxide, where isolated, monomeric structures predominate. This project combines the synthesis of catalyst materials using atomic layer deposition (ALD), catalytic performance and kinetics experiments designed to evaluate these materials, and in-situ UV resonance Raman spectroscopy to monitor changes in the catalyst and the nature of surface reactants and products during the reaction. We are particularly interested in understanding the acid-base nature of oxides synthesized by ALD. Adsorption of molecules that probe surface acidity, such as pyridine, can be employed to distinguish Lewis and Bronsted acid sites and determine their population. The ALD method has successfully synthesized ultra-uniform TiO_2 monolayers supported on silica and ultra-small iron oxide clusters in zeolites. The iron oxide clusters show exceptional activity for the reduction of NOx in a simulated engine exhaust. UV Raman spectroscopy has also been used to study the formation of coke by acid sites in zeolites. The spectra reveal a complex chemistry in the coke formation process with the formation of unstable and transient intermediates that have not been previously detected or identified.

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

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RESEARCH GOALS AND SPECIFIC OBJECTIVES

Model, elaborate, understand, and exploit pathways by which organometallic molecules of varying nuclearity undergo chemisorptive activation and activity enhancement on solid surfaces. Such processes connect to real-world industrial processes and to manufacturing cleaner, greener, more environmentally acceptable products, including those from renewable resources. Research combines catalyst synthesis, surface chemistry, homogeneous analogue catalysis, and computation, and involves collaboration with national labs and industry. Objectives are (1) investigate/understand organometallic molecule chemisorption on “super Brønsted acid” oxides, (2) develop/understand chemisorption and catalysis by mononuclear and polynuclear species, and (3) characterize new, efficient energy storage materials.

DOE INTEREST

This project relates directly to the efficiency, selectivity, and “greenness” of real-world industrial catalytic processes that are currently practiced on a huge scale, and to the ability of these processes to produce cleaner, more environmentally acceptable products. This includes processes using renewable bio-feedstocks, such as polyethylene production from sugar cane, and those which produce high-capacity energy storage materials.

PROGRESS

Nuclearity Effects on Catalyst Activity and Selectivity: The syntheses of bimetallic group 10 polymerization catalysts were realized, along with their mononuclear analogues. The binuclear catalysts exhibit large increases in ethylene polymerization activity versus monometallic analogues, and increased branching and methyl branch selectivity. Binuclear catalyst-mediated copolymerizations with ethylene + polar norbornenes exhibit a 4x increase in comonomer incorporation, while ethylene + methylacrylate or methylmethacrylate copolymerizations incorporate a 11% acrylate, while the mononuclear catalysts incorporate negligible amounts. The mechanism of these marked cooperative effects was elucidated.

Heterogeneous Catalytic Synthesis of Energy Storage Materials: A series of 0-3 metal oxide-polyolefin nanocomposites were synthesized via in-situ olefin polymerization using the single-site catalysts. The resulting composites were structurally characterized by X-ray diffraction, SEM, TEM, ^{13}C NMR, and DSC. The energy storage densities of these nanocomposites are as high as 9.4 J/cm^3.

Metal Hydrocarbyl Chemisorption on Sulfated Metal Oxide Surfaces: Electrophilic Zr surface alkyls are created in high coverages by chemisorptive protonolysis of group 4 alkyls, and these species exhibit extreme activity for arene and olefin hydrogenation as well as for olefin polymerization. Benzene hydrogenation rates exceed that of any catalyst yet discovered. The kinetics and mechanism were characterized, revealing that ~ 97% of the surface Zr species are catalytically significant—unusual for any heterogeneous catalyst. EXAFS studies with Drs. N. Guo and J. Miller of Argonne National Laboratory indicate, for Cp^*ZrMe_3/AlS where ~ 95% of the Zr sites are catalytically active, that the $Cp^*ZrMe_2^+$ cation essentially “floats” above the AlS$^-$ surface with very weak ion pairing.

Investigation of the Nature of Active Sites on Heteroatom-Containing Carbon Nano-Structures for Oxygen Reduction Reaction

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GOAL

This project is aimed at the development of non-noble metal electrocatalysts for fuel cells, while investigating the active sites involved in the catalytic phenomena that govern the oxygen reduction reaction. Identification of active sites would then help tailor better performing catalysts with higher stability by incorporating changes in the molecular structure and graphitization of the carbon nano-structured catalysts.

DOE INTEREST

The significance of this project arises from the need to develop platinum-free oxygen reduction reaction (ORR) electrocatalysts for proton exchange membrane (PEM) fuel cells. Although it is believed that nitrogen contained in the carbon of carbon nano-structured (CNx) catalysts facilitated ORR, more insight is required for a fundamental understanding of the role of heteroatoms as active sites for the reaction. By exploring the nature of active sites and ORR mechanism on these heteroatoms incorporated in carbon-based catalysts, these materials could be tailored to create more active and stable catalysts by generating changes in surface moieties. Another important objective of this project is to integrate electrochemistry with heterogeneous catalysis, the amalgamation of which will be beneficial for both fields in the long-term.

RECENT PROGRESS

Investigating the Active Site by Selective Poisoning Experiments

CO Poisoning: The effects of CO on ORR activity of Pt and carbon nanostructures (CNx) were observed in half-cell electrochemical experiments. When CO and O_2 were simultaneously bubbled through an acidic solution, Pt catalyst was seen to selectively adsorb CO, thus ceasing any oxygen reduction activity. This effect was not seen for CNx catalysts, which showed a drop in oxygen reduction activity due to a displacement effect of oxygen, and resumed ORR activity as soon as CO was stopped from bubbling into the solution. CO pulsed chemisorption as well as Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) experiments showed an uptake of CO by platinum, but no uptake was observed with CNx.

Cyanide Poisoning: Cyanide poisoning of Pt and CNx was carried out by dissolving potassium cyanide in the electrolyte for half-cell experiments. Pt showed immediate deactivation upon introduction of CN-, but no deactivation was observed in the case of CNx catalysts.

Probing the Pyrolytic Growth of Fe and Co Containing Carbon Nanostructures under Operando Conditions with EXAFS

In order to understand the changes in the metal phase of the growth catalyst for ORR-active carbon nanostructures, operando pyrolysis experiments were performed by obtaining X-ray absorption spectra during pyrolysis. It is seen that iron changes its state from oxide to a more reduced metallic phase upon heat treatment to 800oC in nitrogen. Characterization using X-ray diffraction (XRD) and transmission electron microscopy (TEM) imaging will yield further insight into the metallic and graphitic phases of the catalysts during pyrolysis growth.

Development of Fe-N-C Catalysts

A new class of catalysts containing iron and nitrogen on high surface carbon supports is currently being investigated. These catalysts are prepared by impregnation of iron and nitrogen into a carbon support with very high surface area, following which it is subject to two heat treatments in an inert gas (N_2 or Ar) followed by ammonia. These catalysts are traditionally known to be unstable under fuel cell conditions, possibly due to dissolution of the metal phase. The effect of acid-washing on the stability of these catalysts to leach out unstable metal sites is currently being investigated.

Mechanistic Studies Aimed at the Development of Single Site Metal Alkoxide Catalysts for the Production of Polyoxygenates from Renewable Resources

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This project involves the development of single site metal catalysts for the ring-opening of epoxdies and cyclic esters in the formation of polyethers and polyesters. In addition we are investigating the copolymerization of epoxides and carbon dioxide to generate a green and sustainable route to polycarbonates as well as the copolymerization of epoxides and organic cyclic anhydrides to make polyesters in an atom efficient manner. The majority of our efforts involve the use of biocompatible main group elements such as Mg, Ca and Zn. Some work also involves the trivalent metals AL, Cr, and Co. Work also involves ligand design to kinetically stabilize the single site activity of kinetically labile metal such as Ca and Mg.

Transition Metal Mediated Transformations of Small Molecules

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Catalysis at metal centers is of great scientific, as well as practical, importance because of the high efficiency, high specificity, and low energy demands often associated with such systems. The two major themes of our research are (1) the design of metal-based systems for the synthesis of novel classes of polymers that incorporate polar monomers and (2) the identification of new metal-catalyzed systems for the conversion of biomass to fuels and chemicals with high specificity. In the process, we expect to address key questions concerning the steps involved in such critical transformations.

The achievement of a fundamental understanding of all aspects of catalysis is an important goal. The Technology Vision 2020 report cites the importance of developing new catalysts for customizing polymer properties. There is also great interest in identifying new technical approaches to the efficient, catalytic conversion of biomass to fuels and chemicals, given the diminishing reserves of fossil fuels - the current commercial sources of fuels and chemicals. The use of biomass substantially reduces net carbon dioxide emissions because the latter is recycled in biomass regeneration. The year 2017 has been set as a target date for replacing 20% of the nation’s petroleum consumption with biofuels.

Fundamental Studies of the Steam Reforming of Alcohols on PdZnO and Co/ZnO Catalysts

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The goal of this project is to elucidate the relationships between the structure and reactivity of Pd/ZnO and Pt/ZnO methanol and Co/ZnO ethanol 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 will determine how Zn alters the activity of Pd and Pt for the dehydrogenation of alcohols and aldehydes and whether reactions on the ZnO support or at the metal-ZnO interface are important. For Co/ZnO the active phase of the catalyst will be determined (i.e., Co, CoO, CoZn alloy, etc.) and again the role of the support will be studied. A surface science approach using model single crystal catalysts (e.g., Pd/ZnO(0001), Zn/Pd(111) and Co(0001)) and an array of surface sensitive spectroscopic probes (HREELS, XPS, LEED, AES, TPD, AFM) will be 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 will also provide fundamental insights that will be useful in understanding a wide range of supported metals catalysts. For example, the research program will investigate 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.

Thermodynamic Properties of Supported Catalysts

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Typical catalytic materials have thermodynamic, redox properties that are very different from that of bulk materials because they 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. 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. Also, in the case of supported metals for Fischer-Tropsch Synthesis, the redox properties of small particles are known to be very different from that of bulk materials. We have developed methods for characterizing the redox properties by coulometric titration and are applying this technique to supported oxide and metal catalysts

Understanding, Harnessing, and Tuning the Catalytic Chemistry of Nonstoichiometric Oxide Surfaces

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A research program is proposed to investigate the catalytic chemistry of nonstoichiometric oxide surfaces. Recently, experiments and theoretical studies have established that simply annealing a complex oxide can yield a surface with a different atomic composition and arrangement than the bulk. Such nonstoichiometric layers often form spontaneously under appropriate conditions, leading to greatly improved catalytic properties. Despite significant work on some aspects, non-stoichiometric surfaces are poorly understood and offer excellent opportunities for understanding relevant catalysts and for discovering more active, selective, and cost-effective catalysts.

The overarching goal of this proposal is to understand, harness, and tune the reactivity of nonstoichiometric surfaces of ABO_3 oxides, with four major research activities:

(1) Despite the parent 1:1 ratio of A and B cations, surfaces enriched in one or the other (as well as variable O concentration) can be formed by annealing, yielding spontaneous, ordered, epitaxial monolayers.The catalytic chemistry of these surfaces will be examined theoretically, focusing on opportunities for highly active and selective chemistry using early transition metals.

(2) Once the chemistry of these overlayers is better understood, the design of new oxides (with different (A1-x Ax)(B1-y By)O_3 composition and/or ferroelectric polarization) can be fruitfully carried out to affect the structure, composition, and electronic properties of the nonstoichiometric surfaces that can be formed on them.

(3) Reactivity studies of the newly-discovered materials and surfaces will be conducted, in a tight materials design cycle.

(4) We will model the systematic introduction of additional elements, including precious-metal incorporation through the “intelligent catalyst” effect and heteroepitaxial growth via atomic-layer deposition. Throughout, the substrate oxide composition and polarization will be varied to affect surface metal properties, focusing on wetting/clustering transitions of the reduced metal as well as catalysis of the oxidized metal incorporated into a nonstoichiometric surface layer."

Catalyst Design by Discovery Informatics

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Funding:	$780,000

The overall goal of this work is to develop a model-based approach to catalyst design that we call Discovery Informatics. The water gas shift (WGS) and single site olefin polymerization reactions serve as development platforms in heterogeneous and homogeneous catalysis, respectively. Specific objectives for the WGS program are to build a database with sufficient chemical and information diversity to allow identification of active sites, to model the kinetics, identify descriptors of the kinetic parameters, and ultimately to use those descriptors to create a predictive model for WGS activity. A combination of accurate steady state and transient kinetic measurements with detailed catalyst characterization using TEM, EXAFS, XANES, and IR, often in the operando mode, for catalysts synthesized on model supports to facilitate the TEM analysis has led us to the working hypothesis. The hypothesis being that for supported Au, the coordinatively unsaturated corner and perimeter atoms at the metal support interface are the dominant active sites, while for Pt all the surface atoms participate. In spite of this substantial difference in behavior, we find that the support plays a deciding role in water activation for both metals and may do so by providing support-specific sites. We have a microkinetic model that accounts for these trends and are now addressing the need to incorporate the coverage dependence of the CO binding energy to the surface. In the coming year we expect to broaden the kinetic models to include additional catalyst types and to use DFT results and scaling rules to develop descriptors for WGS by supported metals.

The overall objectives for the single site polymerization work are similar to those for WGS, but the single site nature of the catalysts provides finer chemical and structural detail. Over the past year we have made significant advances in establishing the standard in the community for how to obtain robust and reliable rate constants for single-site olefin polymerization catalysts. The most stringent requirement is satisfying the molecular weight distributions at different monomer conversions, in addition to monomer consumption, end group analysis, and active site counting. This approach of fitting multi-response data sets guarantees a well defined kinetic mechanism and meaningful rate constants for all the relevant steps, allowing true structure-function understanding. Such understanding is the essence of Discovery Informatics and is an absolute requirement for designing a catalyst from first principles. In our recent work, we have demonstrated the viability of our method and corrected the literature on Brintzinger's catalyst, established direct comparisons for coordination catalysts, and contrasted Zr versus Hf. In one study, we discovered that the pendant ligand, NMe_2 versus THF, has a large effect on the rate constant for chain transfer, kCT. We have shown quantitatively that the rate constant for propagation, kp, for Hf is 20 times slower than that for Zr, resulting in more chain termination and not because kCT is significantly different for the two metals. We are well on our way to completing kinetic analysis of the catalyst systems outlined in the proposal, and we are starting to build structure function relationships that can enable the running of the inverse model to identify optimum catalysts. Finally, we are expanding application of our kinetics toolkit to the case of catalyzed polylactide synthesis in collaboration with the Waymouth group at Stanford.

Fundamental Studies on the Kinetics of Oxidation Reactions

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The overall goal of this work is to study the mechanism and to identify the active sites of Au/TS-1 catalysts for the gas phase epoxidation of propylene in the presence of hydrogen. We investigated the effect of preparation conditions (deposition-precipitation) in the catalytic performance of Au/TS-1 and found that high gold atom efficiency could be obtained on samples with very low gold loading (<0.06wt%). This suggests that the active gold sites for PO reaction are very small (< 1 nm), significantly smaller than the generally accepted optimum gold nanoparticle sizes, which ranges from 2 to 5 nm in many reactions. To probe the location of the active Au clusters, a TS-1 support coated with an inert layer of silicalite-1 (S-1) was designed and prepared to examine the activity of the gold clusters inside the TS-1 nanopores. Since neither Au nor Ti alone gives significant PO activity, any significant PO activity observed from Au/S-1/TS-1 must come from the intimate Au-Ti contact inside the TS-1 core. We found that the PO rate per gram of catalyst of the Au/S-1/TS-1 sample was at least 50 times higher compared to that of an Au/S-1 sample, which suggests that the gold clusters inside the TS-1 are active for the PO reaction. Finally, we attempted to increase the number of active sites by increasing the population of small gold clusters inside the TS-1 by preparing the Au/TS-1 catalyst using Cs_2CO_3 as the precipitation agent. We found that Cs could further promote the initial PO rate of Au/TS-1 up to 2 times higher than the highest PO rate reported to date. A combination of material design experiments, XPS and TEM analysis reveals that there exists a special Au and Cs interaction, which is induced by the presence of the nanoporous structure in the TS-1. We propose that the enhanced PO activity of the Cs promoted Au/TS-1 catalyst is attributed to the stabilization of the gold clusters inside the TS-1 nanopores by the presence of cesium.

Oxo Catalyst for the Conversion of Lignocellulosic Biomass

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Plants are solar factories that utilize carbon dioxide, water, and sunlight to make lignocellulosic matter. Unfortunately, biomass is not a good fuel because of the high oxygen content in lignin and cellulose, which contain one or more oxygen atoms per carbon. The challenge for making hydrocarbon fuels from biomass is two-fold: (1) unraveling the biological polymer and (2) removing the oxygen atoms. We have discovered that the water soluble methylrhenium trioxide (MTO) catalyzes the conversion of diols to alkenes (DARe) with dihydrogen under reasonable conditions. MTO is effective for aliphatic, cyclic, and aromatic diols with high selectivity for olefins. It also gives good yields of alkene (60-70%) with cyclic cis diols. The kinetics and reaction mechanism have been under investigation. We have also been extending the diol-to-alkene reaction to carbohydrates and polyols from biomass feedstock. Based on mechanistic knowledge and understanding we proceed with intelligent catalyst design that would lower the energy barriers (improve reaction kinetics) and enhance catalyst stability.

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

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We have constructed a database of computationally-predicted zeolite-like structures. To date, we have roughly 2.7 million structures in this database, with roughly 10% within the 30kJ/mol Si energetic band above a–quartz in which the known zeolites lie. This number is to be compared to the roughly 190 structures of known zeolites. Predicted structures within this band have geometric and topological characteristics similar to that of known zeolites. Known zeolites were shown to lie on the low-density edge of the distribution of predicted structures. Dieletric constants and X-ray powder diffraction patterns were calculated. The structures were deposited in two publicly available databases. This work was featured on the covers of J. Chem. Phys. C and Phys. Chem. Chem. Phys.

This database is now being screened by colleagues at Georgia Tech (David Scholl), Berkeley (Berend Smit), Northwestern (Randy Snurr), BASF, Chevron, and others. As example properties, we have calculated low and high frequency dielectric constants. We have also calculated elastic modulii. And we have calculated density, coordination sequences, and ring distributions.

Even just in the area of carbon capture materials, zeolites show a tremendous potential for improve throughput and selectivity versus polymeric systems. A very limited subset of the database of new zeolite-like materials has been screened, with already a number of better-performing materials found. It goes without saying that zeolites are currently used on a massive scale in energy-related applications. Understanding zeolite nucleation is important not only scientifically for the discovery and synthesis of new materials, but also in an engineering sense for improving the performance of existing materials that are not performing as well as they could due to poor "crystallinity." Considerations include catalysts with improved catalytic properties for improving refining economics and for reducing environmentally-unfriendly by-products, design of better, smarter, and more energy-efficient separation processes, and design of zeolites that are more effective for radioactive waste cleanup and stewardship purposes.

It is our long-term goal that structures from this database will be identified by their predicted material properties and become the subject of targeted synthesis by our experimental colleagues. We also look forward to collaboration with our theoretical colleagues to screen the database for interesting and useful physiochemical functions. For example, in collaboration with Berend Smit, we will begin to address the calculation of catalytic materials properties. The strategy we will follow when considering a set of industrially interesting transformations is to list all known mechanisms with intermediate states for performing the transformation. By examining the physical constraints that the zeolite places upon the reactions, we can determine which are feasible. In this way, we can rank the hypothetical frameworks for likely performance on the transformation.

Deem was awarded the Professional Progress Award of the AIChE, elected to fellowship of AAAS, and received the 2012 O'Donnell award of TAMEST.

Group Transfer Reactions by Inexpensive Transition Metals

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This project aims to explore the catalytic ability of low-coordinate cobalt complexes in small-molecule catalysis. Cobalt is of great interest because it is inexpensive and nontoxic, and shows promise for replacing precious metals for organometallic transformations. As a first-row metal, cobalt complexes with a low coordination number have a high-spin electronic configuration, which enables new pathways and mechanisms. In this project, we will demonstrate organometallic transformations such as hydrogenation and hydrosilylation, determine the mechanisms of these transformations, and explore novel outcomes and selectivities.

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

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This project is directed towards fundamental investigations of the reactions of homogeneous transition metal complexes with aliphatic and aromatic hydrocarbons, saturated and unsaturated, and their simple functionalized derivatives (e.g., carbonyl, nitrile, halides). Our studies provide fundamental information about the mechanisms and reactivity of metal complexes with C–H, C–C, and C–X bonds in a wide variety of hydrocarbons. The key to understanding reactivity of these molecules lies in determination of the kinetic and thermodynamic selectivity for cleavage of these bonds by coordinatively unsaturated metal species. Determination of metal-carbon bond strengths is critical to understanding the thermodynamic factors that control the reactions. Knowledge of the role that alkane sigma-complexes play in alkane activation and the dynamics of interconversion of these species can be used to predict and understand their preference for terminal C-H activation. New substrates for the cleavage of C–C bonds will be sought extending the examples to include sp, sp2, and sp3 hybridized carbon. New metal complexes for cleaving these bonds will be found. The interplay between eta2-coordination, C–H oxidative addition, and C–C oxidative addition will be applied to the cleavage of C–C linkages. We will look extensively at C-CN cleavage in a variety of nitriles in order to determine how these C-C bonds can be cleaved so easily, and to see if the kinetic access to these bonds can be extended to other systems. In particular, we want to understand why rhodium prefers C–H cleavage whereas nickel prefers C–C cleavage. We will also develop new catalytic systems for the functionalization of C–C bonds, including hydrogenolysis, carbonylation, olefination, carbosilation, and acetylene insertion reactions. The cleavage of strong C–F bonds by early transition metal hydrides in olefinic, and aromatic fluorocarbons will be investigated and the mechanism of these C-F cleavages determined. In all of these areas, we will apply DFT theory to examine stabilities of reactants, intermediates, and transition states, providing a comprehensive understanding of strong bond activation.

The success of this work will lead to new approaches for the manipulation of petroleum-based hydrocarbons and functionalized derivatives. New processes for making and breaking strong bonds in organic molecules will be based upon the lessons learned from the kinetic and thermodynamic studies of the type presented here. The work has the potential to have a significant impact in science and in technologies of interest to DOE as the chemistry relates to the petroleum industry and chemicals derived from petroleum.

Nanoscale Surface Chemistry: Over Faceted Substrates: Structure, Reactivity and Nanotemplates

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Our overall research goals are to investigate new aspects of the relationship between nanoscale surface features and heterogeneous chemistry as well as electrochemistry. Our emphasis is on atomically rough morphologically unstable surfaces of catalytic metals [fcc Ir(210), hcp Ru(11-20), Ru(11-21), Re(11-21) and Re(12-31)] that can undergo nanoscale faceting upon annealing in O_2, NO_2 and C_2H_2 or covered by monolayer Au followed by annealing. The focus of our work is on the structure of faceted surfaces, reactivity of faceted surfaces in catalytic reactions and electrochemical reactions related to air pollution control and hydrogen production, and the use of faceted surfaces as nanotemplates for growth of metallic nanoclusters and synthesis of nanoscale model electrocatalysts.

Our specific objectives are to (a) identify the causes of faceting and other nanometer-scale growth phenomena on adsorbate-covered faceted surfaces and (b) correlate surface structure and surface (electro)reactivity with nanometer-scale features.

Our significant achievements and results since our last report are as follows:

(1) The discovery of C-induced faceting of Re(11-21). We have also identified shapes and orientations of the facets formed on faceted C/Re(11-21). This is the first observation of C-induced faceting of a Re single crystal.

(2) The successful synthesis of nanostructed model electrocatalyst of Pt monolayer (ML) supported on faceted C/Re(11-21) with novel activity for hydrogen evolution reaction (HER). This is the first application of a faceted metal surface as a nanotemplate to synthesize nanoscale model Pt electrocatalyst with well-defined surface structure and controlled size on the nanometer scale, which can bridge the gap between supported Pt nanoparticles and Pt single crystals. The ML Pt supported on C/R nanotemplate exhibits higher activity for HER than commonly used pure Pt.

(3) Exploring the origin of the higher reactivity of planar Ir(210) for oxidation of CO to CO_2 by pre-adsorbed NO or O than that of faceted Ir(210). TPD data suggest the same reaction pathway for CO_2 formation from CO+NO and CO+O reactions on planar Ir(210). DFT calculations reveal that, compared to much higher O diffusion barriers on the faceted surface, planar Ir(210) facilitates one-dimensional O diffusion that might cause the higher reactivity for CO oxidation on planar Ir(210).

(4) Clear evidence has been found for structure sensitivity in reduction of NO by pre-adsorbed C_2H_2 on faceted Ir(210) versus planar Ir(210), but no evidence has been found for size effects in this reaction on faceted Ir(210) for average facet size ranging from 5nm to 14nm.

(5) The finding of O-induced faceting of Ru(11-21). The morphology of faceted O/Ru(11-21) is substantially different from that of faceted O/Re(11-21). Our work demonstrates that clean faceted Ir(210) offers an opportunity to quickly screen size effects in surface reactions over iridium without changing samples. In addition, our findings of nanoscale model Pt electrocatalyst with novel

electrochemical activity for HER illustrate the potential for future studies of nanostructured bi-metallic systems that not only largely reduce the use of Pt but also improve the activity for HER. The results indicate that further detailed experimental and theoretical studies of surface chemistry on nano-faceted metal surfaces and electrochemistry over Pt ML supported on faceted metal surfaces are necessary to elucidate the role of nanometer scale features in the high activity during the chemical and electrochemical reactions, an important issue in catalysis.

The potential impact in science and technologies of interest to DOE is that our results provide new understanding of dynamic structural rearrangements at the surfaces of high area metallic catalysts, and are clarifying the role of nanometer-scale size effects in environmental-related surface reactions such as reduction of NO and oxidation of CO as well as energy-related reactions such as the hydrogen evolution reaction.

Enabling Catalytic Strategies for Biomass Conversion

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Funding:	$160,000

The objective of the proposed research is to develop selective catalytic processes for converting bio-feedstocks into new classes of value-added chemicals and thermoplastics. The research project targets the development of new families of biomass-derived commodity chemicals will enable a variety of technology options for transforming biorefinery products into value-added commodities to increase the sustainability of future biorefineries.

Specific aims are to develop selective catalysts for converting biorefinery feedstocks such as glycerol, 3-hydroxy propionic acid, and furan dicarboxylic acid into new families of chemical intermediates and high performance thermoplastics. Our experimental approach is to develop an integrated platform of selective catalysts for converting biomass-derived feedstocks into value-added chemicals and polymers. An integrated approach will entail conversion of biomass-derived feedstocks to monomers that can be polymerized to thermoplastics that can replace existing thermoplastics with competitive materials derived from biomass.

A representative example of our approach is the generation of a new family of polycarbonates derived from the readily available biorefinery co-product glycerol. This strategy entails the selective conversion of glycerol into dihydroxyacetone and the conversion of dihydroxyacetone into novel families of polycarbonates. These objectives are guided by the hypothesis that the polycarbonates derived from dihydroxyacetone would exhibit properties of high-performance thermoplastics, based on structural analogies to related petrochemically-derived polyketones such as CarilonTM, an alternating copolymer of ethylene and carbon monoxide.

To achieve these objectives, we have developed two new catalytic processes as part of a catalytic platform to convert the three-carbon feedstock glycerol into new families of polycarbonates. The first catalytic process entails a palladium-catalyzed selective oxidation of glycerol to dihydroxyacetone. The selective, catalytic aerobic oxidation of glycerol discovered in our group provides a promising strategy for converting glycerol, a biorefinery biproduct, to useful commodity chemicals. We have demonstrated that the catalytic oxidation of glycerol can be carried out in water. This is an important advance, since glycerol is typically produced as a 12 wt% aqueous solution in biorefineries. The direct oxidation of aqueous crude glycerol might provide strategies for avoiding energy-intensive purification of glycerol by distillation.

To convert dihydroxyacetone into polycarbonates, we are investigating strategies based on the ring-opening polymerization of cyclic carbonates. As the cyclic carbonate of dihydroxyacetone is unknown, we have adopted an indirect approach involving the formation of dihydroxyacetone acetal and its corresponding cyclic carbonate. We developed a catalytic strategy for the direct oxidative carbonylation of diols to generate cyclic carbonates. This is an important advance, as the standard procedure for generating polymerizable 6-membered carbonates involves phosgenation of 1,3-diols, but the hazards associated with phosgene-derived reagents limit the attractiveness of this approach.

With an expedient synthesis of cyclic carbonates in hand, we have utilized our recently developed organic catalysts for the ring-opening polymerization of the cyclic carbonates to generate the polycarbonates of dihydroxyacetone. Initial investigations of this polycarbonate reveal it to have a melting point above 200 °C. We have also generated several families of copolymers to generate a range of polycarbonates with different physical properties.

The successful generation of new families of polycarbonates is one example of a general strategy experimental approach to expand our technology options for converting biomass-derived feedstocks into value-added chemicals and polymers.

Catalytic Hydrogenation of Carbon Monoxide and Hydrocarbon Oxidations

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Development of new reaction strategies and catalyst materials to produce organic oxygenates from small molecule substrates is a unifying theme for this program that broadly encompasses reactivity, kinetic-mechanistic, and thermodynamic studies for organo-metal directed processes. Formation of organic oxygenates by oxidation of hydrocarbons, hydration and alkoxylation of alkenes, and reduction of carbon oxides are several current specific objectives. One of the major interests is to develop and evaluate strategies to obtain selective catalytic oxidations of olefins to form aldehydes, ketones, epoxides, and 1,2 diols. Group nine metallo-porphyrins and related macrocyclic complexes are applied as prototypical metal species for illustrating substrate reactivity, mechanistic pathways, and equilibrium thermodynamic measurements relevant to metal-organic bond energetics. Regioselectivity for reactions of metalloporphyrin derivatives with olefins suggests approaches to form primary alcohols and ethers from addition of water and alcohols with olefins. Another central objective of this program is to explore new strategies to produce organic oxygenates from carbon monoxide. The general approach is to design catalytic cycles that take advantage of the highly unusual reactions of group nine macrocyclic complexes that reduce and couple carbon monoxide in dimetal ketones (M-C(O)-M) and dimetal ketones (M-C(O)C(O)-M), and reactions of CO and H_2 that produce metalloformyl (M-CHO) and hydroxymethyl (M-CH_2OH) species. Current emphasis is focused on evaluating tethered dirhodium(II) diporphyrin complexes that selectively react with CO to form metalloketone and dimetaloketone species. Variation of the reaction medium is being systematically developed as a means to attain selectivity by tuning the reaction pathway and thermodynamics.

Nanostructured Metal Oxide Catalysts via Building Block Syntheses

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The main goal of our DOE funded research project is to develop a general synthetic methodology for the preparation of nanostructured, single site heterogeneous catalysts. The strategy that we have pursued involves three components: (1) finding a suitable building block that will function as the main structural component of the support, (2) finding a broad class of linking reagents that insert catalytic centers into the matrix or linking groups that make the matrix more chemically and thermally robust, and (3) finding a simple, clean linking reaction that allows us to bond building blocks with linking reagents and produce the desired catalysts. In addition to these components and general linking reaction, we have also developed the method of sequential additions which allows us to vary the number of covalent bonds that link an active site to the support. The connectivity of a metal to the support is one of the most important attributes that defines a metal site and ultimately its properties in application to catalysis. The general precepts of this strategy are described in two recent publications (Catal. Today 2011, 160, 153; Chem. Mater. 2007, 19, 3212).

In FY 2011 work has focused on two main areas of investigation:

(1) A family of titanium in silica catalysts has been prepared in which each member of the family exhibits a different connectivity of titanium to the matrix. Specifically, we have prepared Ti-Si_8O_{20}silicate matrices in which the atomically dispersed titanium cations are bound to the surrounding cubic Si_8O_{20} building blocks by 1-, 2-, 3-, or 4-bonds (referred to as 1-connected, … 4-connected centers). In the past year we have investigated the reactivity of each of these distinct materials as catalysts in the peroxide oxidation of trimethylphenol to the corresponding benzoquinone. We have found that the 2C-Ti catalyst is three to five times more active on a per site basis than either the 3C- or 4C-titanium containing materials. These are the first clear, well defined examples that we are aware of in which a direct correlation between the connectivity of a metal to the support and catalytic activity has been demonstrated. Current work is focused on determining if these differences persist when traditional high temperature procedures are applied to these materials or does calcination “homogenize” the sites in these matrices.

(2) The second focus of effort in the past year has been to characterize the aluminum sites that develop in the reaction of $AlCl_3$ with the cubic building block, Si_8O_{20} $(SnMe_3)$8. Normally, trimethyltin chloride is the only byproduct observed when links between aluminum (or any other metal chloride reagent) and the Si_8O_{20} cube are formed, but in this case significant amounts of tetramethyltin is observed. The observation of tetramethyltin clearly indicates that a new reaction is operative and this makes it hard to define what the aluminum site looks like in the building block matrix. In the past year we have broadened our efforts to include two other members of this family: gallium and boron. $GaCl_3$ reacts

similarly to aluminum in that tetramethyltin is again observed, but in the case of boron, no $SnMe_4$ is observed. Furthermore when pyridine is present, no $SnMe_4$ is produced in any of these systems nor is it observed with POSS analogues to the octatin cube are used. Our efforts to define the aluminum, gallium and boron sites in these matrices continue.

New Horizons in C-F Activation by Main Group Electrophiles

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Funding:	$143,000

This project expands a novel approach to activation and functionalization of C-F bonds. The key innovative aspect is the departure from the transition metal paradigm in C-F activation. While the thrust of much of the research in the area of well-defined C-F functionalization is in the direction of using electron-rich transition metal complexes, this project relies on an electron deficient main group catalyst and the process does not involve redox changes. Carbon-fluorine bonds are among the most robust functionalities in chemistry owing to their thermodynamic stability and kinetic inertness. Activation of C-F bonds is thus a fundamental challenge of note. It is also often viewed through the prism of remediation of polyfluoroorganic atmospheric pollutants such as chlorofluorocarbons (CFC), hydrofluorocarbons (HFC), and perfluorocarbons (PFC), all of which are very potent greenhouse gases. They are entirely anthropogenic and their sources (as waste) include some key industries, such aluminum, magnesium, and semiconductor production.

Our chemistry utilizes highly reactive main group cations (silylium 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).

In FY2011, the focus has been 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 originally employed halogenated carboranes, such as $[HCB_{11}H_5Cl_6]$-, $[HCB_{11}H_5Br_6]$-, and $[HCB_{11}Cl_{11}]$-. Their intrinsic suitability for the catalytic process was excellent, but the cost was high and the solubility rather low. We have now developed new, convenient syntheses of electronically similar carboranes that possess increased solubility. In particular, we have developed (1) reliable carborane chlorination procedures that do not use chlorine gas, (2) a procedure for C-alkylation of $[HCB_{11}Cl_{11}]$- resulting in much more soluble $[Alkyl\text{-}CB_{11}Cl_{11}]$- anions, and (3) syntheses of mixed triflate/halogeno-substituted carboranes with substantially improved solubility. In addition, we have developed a new, much more practical method for the synthesis of $[B_{12}Cl_{12}]$2- dianion and showed that it is capable of supporting HDF with turnover numbers as high (>103) as with carboranes. $[B_{12}X_{12}]$2- dianions are much more synthetically accessible and thus cheaper than their carborane relatives.

In order to facilitate our understanding of the mechanism of the electrophilic C-F activation, we continued our collaboration with Professor Dmitry Gusev (Wilfrid Laurier U, Canada). Our new calculations explored the comparative stability of the adducts of the active silylium catalyst with compounds typically present in the catalytic reaction mixture. Initial computational studies aimed at further insight into the mechanism suggested that Si-H containing siloxanes can be superior sources of H in hydrodefluorination. Fortuitously, oligo- and polymethylsiloxanes (MeSiHO)n are also among the cheapest sources of Si-H. Preliminary experiments have already demonstrated that polymethylsiloxane is a viable stoichiometric reagent in HDF catalysis.

The Physical and Chemical Properties of Nanostructured Mixed-Metal Catalysts

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Funding:	$220,000

A methodology has been developed for the synthesis and characterization of planar SiO_2-supported Pt and Rh model catalysts at ultrahigh vacuum and at elevated pressures using Auger electron spectroscopy (AES), temperature programmed desorption (TPD), and infrared reflection absorption spectroscopy (IRAS). This synthesis approach allows supported metal nanoparticles to be prepared with well-defined particle sizes and narrow size distributions. These model catalysts have, in turn, been used to investigate structure-activity relationships of Pt and Rh nanoparticles for important structure-sensitive reactions, e.g., alkane dehydrocyclization, alkene disproportionation, and dehydroformylation. The results indicate the relative importance of low-coordination sites and electronic effects as a function of particle size in determining catalytic activity and selectivity. The insights gained from these oxide-supported model systems bridge the material gap between single crystal and technical catalysts, and provide an additional level of complexity while maintaining complete access to the broad spectrum of modern surface science techniques.

Modeling Catalyzed Growth of Single-Wall Carbon Nanotubes

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Funding:	$106,000

OVERALL RESEARCH GOALS

This project aims to provide new insights into the catalyzed growth of single-wall carbon nanotubes (SWCNTs). In previous years (2004-2006), under an NSF/NER grant, we initiated a series of computational studies oriented to identify the main aspects of nucleation and growth of SWCNTs produced by decomposition of a precursor gas on supported metallic nanoclusters. In particular we were interested in the CoMoCAT synthesis process from Resasco et al, our collaborator in the NER grant, which utilizes Co nanocatalysts supported on a Mo carbide surface at 750oC and pressures from 2-5 atm. Our current main objectives are to (a) identify the role of morphology, size, and chemical composition of the supported catalyst on the precursor decomposition and initial stages of C deposition and reaction; (b) identify the role of the cluster-substrate interactions to determine a given nanocluster morphology and size distribution; and (c) determine the effect of the cluster morphology and chemical composition on the reactivity of growing caps of different chiralities.

SPECIFIC OBJECTIVES FOR THE PREVIOUS YEAR

The objectives were to determine the influence of the surface pattern on the growth of specific carbon structures, the effect of catalyst composition on carbon adsorption and absorption, the effect of catalyst size and metal-substrate interactions on the competition between growth and catalyst poisoning, and the formation of double-walled carbon nanotubes.

SIGNIFICANT ACHIEVEMENTS AND RESULTS FOR THE PREVIOUS YEAR

Influence of the Surface Pattern on the Growth of Specific Structures: Our DFT studies demonstrated the existence of an inverse template effect during the growth of carbon nanotubes using floating catalysts. Classical MD simulations using a reactive force field proved the influence of a strongly interacting substrate on the structure of a metal nanocatalyst and illustrated how such interaction may help preserve catalyst crystallinity. DFT optimizations of carbon structures on stepped (211) and (321) cobalt surfaces showed the template effect imparted by the nanocatalyst surface on the growing carbon structure at early stages of nucleation. It was found that depending on the step structure and type of building block (short chains, single atoms, or hexagonal rings), thermodynamics favor arm-chair or zig-zag termination, which provides guidelines for a chirality-controlled process based on tuning the catalyst structure and the type of precursor gas. Additional MD studies were used to prove the existence of a surface template for intermediate chiralities (between arm-chair and zig-zag).

Effect of Catalyst Composition: We investigated the effect of bimetallic and trimetallic compositions on C adsorption and absorption. The surfaces investigated belong to the group of Fe2Al-X (with X = Nb, Ti, and V) that have technological interest because of their anticorrosive properties.

Effects of Catalyst Size and Metal-substrate Interactions on the Growth of Single-walled Carbon Nanotubes: We developed a simple model combining thermodynamic and kinetic effects to identify regions of single-wall carbon nanotube growth in the phase space defined by work of adhesion, temperature, and catalyst size. We constructed a growth diagram in the space of metal-substrate vs. metal-carbon strengths of adhesion, defining regions of nanotube growth and encapsulation. In the growth region, we identified zones of higher or lower quality of the nanotubes grown. This theoretical characterization is very useful to guide a controlled synthesis.

Potential Impact in Science and in Technologies of Interest to DOE: We expect that our studies will contribute to the understanding of selective nanotube growth, one of the current outstanding challenges in the use of SWCNTs. In addition, fundamental studies of carbon nucleation and growth may provide new insights for the design of other catalytic processes.

Theory-Guided Design of Nanoscale Multi-Metallic Catalysts For Fuel Cells

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Funding:	$200,000

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 effort 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 understand the evolution of the catalytic structure and its long-time behavior.

Thus, the main objectives of the work done under this grant here can be outlined as:

(a) Perform characterization of the time evolution of the catalytic structure and dynamics of nanoalloys under increasing oxidative or reductive atmospheres.

(b) Perform analysis and characterization of the reactivity of porous nanostructures after dealloying occurs as a consequence of surface segregation/dissolution.

(c) Conduct a series of theoretical electron transfer and transport calculations along with selected STM experiments, designed to help in the understanding of the observed electron transfer phenomena due to confinement. This activity is based on our hypothesis that metal porous nanostructures arising after surface dealloying have special reactivity features associated with electronic and geometric confinement, that we have proved in preliminary recently published work. We expect this work to impact not only the specific reactions of this study, but a more general group of reactions that we envision will emerge from this new perspective.

Potential impact in science and in technologies of interest to DOE: This research will allow design of catalysts for the oxygen reduction reaction with improved activities and durabilities; simultaneously advancing the fundamental and applied aspects of catalytic reactions such as the physics, chemistry, methods, and development of accurate guidelines for rational design.

Correlation of Theory and Function in Well-Defined Bimetallic Electrocatalysts

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Funding:	$496,000

The objective of this research proposal is to correlate the structure of nanoparticles that are comprised of ~100 atoms to their catalytic function. The project is based on a growing body of evidence suggesting that catalytic properties can be tailored through controlled synthesis of nanoparticles. What is missing from many of these studies, and what we are contributing, is a model catalyst that is sufficiently small and well-characterized that its function can be directly predicted by theory. Specifically, our work seeks to develop a fundamental and detailed understanding of the relationship between the structure of nanoscopic oxygen-reduction catalysts and their function. We have assembled a team with expertise in theory, synthesis, and advanced characterization methods to address the primary objective of this project. We anticipate the outcomes of the study to be (1) a better theoretical understanding of how nanoparticle structure affects catalytic properties; (2) the development of advanced, in-situ and ex-situ, atomic-scale characterization methods that are appropriate for particles containing about 100 atoms; and (3) improved synthetic methods that produce unique nanoparticle structures that can be used to test theoretical predictions.

During the past year we have made three significant advances that are consistent with the original goals of this project. First, we have fully integrated our experimental and theoretical studies. This has taken some time to accomplish, but now members of our two groups have learned how to communicate and work together in the space where theory and experiment overlap. This is demonstrated by our extensive progress in understanding how core@shell DENs form during electrochemical underpotential deposition. Second, we have developed in-situ X-ray absorption spectroscopy methods and have shown that there are minimal structural changes to monometallic dendrimer-encapsulated nanoparticles during the oxygen reduction reaction (ORR). This is a critically important finding, because effective correlation of the theory with experiment requires knowledge of the structure of the catalytically active nanoparticles. Finally, we have developed a new microfluidic tool for measuring ORR kinetics. The microfluidic system is much more effective for our studies than alternative methods, because it can measure faster kinetics under a broader range of conditions.

Surface Chemical Studies of Gold Model Catalysts

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Funding:	$145,000

Gold nanoparticles have shown remarkable size-dependent properties in catalyzing environmentally-important and industrially-relevant chemical reactions under relatively mild conditions. We propose to study surface chemical reactions on model gold catalysts using ultrahigh vacuum surface science techniques. In particular, the primary gold model catalyst surfaces we will study include (1) planar wafers of a metal oxide [TiO_2 (110) and CeO_2 (111)] decorated with gold clusters and (2) metal oxide nanoparticles (ceria and titania) dispersed on a Au(111) surface [so-called inverse model catalysts]. We propose three major surface catalytic themes regarding the chemistry of these model gold surfaces that build on our experience from the recent past: (1) the water gas shift reaction and the influence and role of adsorbed water in CO oxidation, (2) the selective catalytic oxidation of ammonia to dinitrogen and hydrogen, and (3) the partial oxidation of alcohols. We will employ molecular beam surface scattering techniques, temperature programmed reaction spectroscopy, and higher pressure steady-state catalytic measurements on our gold model catalyst surfaces. We will synthesize gold model catalyst surfaces employing two methods: (1) simple evaporation of the nanoparticle material onto a substrate as well as (2) using a magnetron sputtering cluster source fitted with a quadrupole mass filter for size-selection in order to deposit size-selected clusters (in the 1-10 nm range) on planar substrates. We will employ reproducibly prepared titania and ceria wafers as supports for the gold clusters in addition to using the Au(111) surface as a support for ceria and titania nanoparticles. We will physically characterize these model catalyst surfaces employing several surface sensitive tools. We will investigate adsorption, reaction, and desorption of molecules relevant to our proposed surface chemical themes on the gold model catalysts and related surfaces [e.g., bare TiO_2]. We expect these studies to shed light on the heterogeneous chemical catalysis of metal-oxide supported gold nanoclusters. Further, the proposed research will impact, more generally, the fundamental understanding of nanoparticle size effects and support effects in surface chemical transformations.

Mechanism-Based Design of Biomimetic Green Oxidation Catalysts

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Funding:	$155,000

The long-term goal of the proposed project is to develop efficient and selective catalytic systems for green oxidations using hydrogen peroxide or dioxygen as oxidants that do not generate environmentally harmful wastes. 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. Non-toxic, biocompatible iron complexes will be used as catalysts acting similarly to natural iron-containing oxidative enzymes. Identification of kinetically competent intermediates (transient, very reactive species) is critical for the synthesis of useful, selective and efficient oxidation catalysts utilizing dioxygen and hydrogen peroxide as terminal oxidants. We propose detailed kinetic and mechanistic studies that will allow us to watch the intermediate formation, and their subsequent reactions with substrates by time-resolved spectrophotometry on a millisecond time scale. In order to obtain mechanistic information relevant to rapid catalytic reactions, the individual reaction steps should also be rapid. Thus, the multi-mixing stopped-flow technique is applicable to the systems of interest, and low temperatures will help to uncover the details of formation and reactivities of short-lived, unstable intermediates. This program will provide much needed information about the details of individual reaction steps in oxygen activation.

The project will focus on both previously known and new iron complexes with aminopyridine ligands that generate iron-peroxo or high-valent iron-oxo species upon reactions with O_2, H_2O_2, and other oxygen donors. Specific reactions include new aromatic hydroxylation that has recently been discovered in the group and olefin epoxidation catalyzed by a new family of mononuclear iron macrocyclic complexes. Both reactions, which are highly selective, utilize H_2O_2 as an oxidant and are amenable to mechanistic studies. The proposed project is aimed at establishing the scope and mechanisms of these reactions, with an emphasis on distinguishing between monometallic and bimetallic peroxide activation. These studies will allow for rational, mechanism-based reagent and catalyst design. Additionally, a family of iron complexes with amide-containing macrocycles will be developed for dioxygen binding and activation.

As an outcome of the proposed studies, a detailed picture of the preferential reactivity of various iron-peroxo and high-valent iron-oxo intermediates will emerge. This knowledge will allow researchers to rationally select suitable intermediates for specific organic transformations (as exemplified by epoxidations and aromatic hydroxylations in the proposal). The ligand structural features that stabilize particular intermediates will be determined, along with the chemical ways of activating less reactive, yet possibly more selective intermediates. The understanding of reactivity profiles of various iron-based intermediates will help to interpret the mechanisms of known catalytic oxidations, as well as provide guidance in future catalyst design.

Nanostructured, Metal-ion Modified Ceria and Zirconia Oxidation Catalysts

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Funding:	$310,000

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 for hydrogen generation. The low temperature water-gas shift and methanol steam reforming reactions are studied on Au, Pt, Cu dispersed on nanoscale ceria, iron oxide, and zinc oxide. Alkali promotion was added to the program objectives last year. The concentration and types of oxygen defects are strong functions of the size, shape, and composition of the oxide nanoparticles. Novel chemical synthesis techniques are employed to control the size and shape of oxide nanoparticles, which in turns controls metal ion stabilization and catalytic activity for the two reactions under study in the project.

The project was motivated by the original reports by the PI's group that the activity of ceria-supported gold or platinum catalysts for the water-gas shift reaction is not due to the presence of the metal nanoparticles. Rather, a sub-structure of oxidized metal atoms and ceria, i.e., Au-O-Ce and Pt-O-Ce ensembles, contains the active sites for this reaction. While the metal particle size distribution is not important, the particle size, shape, and oxygen defect density of the host oxide (ceria) are crucial for an active water-gas shift catalyst. These results have a major impact on catalyst design and development.

The extension of these findings to other fuel processing reactions, such as methanol steam reforming, is of interest. Also under investigation in this project are other nanoscale oxide hosts, such as zirconia, iron oxide, and zinc oxide. Since the last report, we have identified that alkali addition can enable the use of silica and alumina supports on which Pt in low amounts (<1 wt%) is rendered as active as Pt on ceria. These findings are exciting and of interest to DOE in that they free the choice of catalyst support from the rare earth oxides to cheap and abundant oxide supports. Lower-cost catalysts for hydrogen generation and purification are critical to the development and market penetration of fuel cells.

Towards a Molecular-Scale Understanding of Photocatalysis on Metal Oxides: Surface Science Experiments and First-Principles Theory

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This combined experimental and theoretical research project continues and extends previous DOE-funded work on the surface (photo-)reactivity of titanium dioxide (TiO_2) and related photocatalytically active semiconducting oxides. TiO_2 is a promising photocatalyst with a wide range of current and prospective applications that are of interest to the DOE mission, mainly the photocatalytic splitting of water to produce hydrogen, the design of high-efficiency solar cells, the remediation of pollutants, and the cleaning of indoor air. A huge amount of work on TiO_2 has been carried out over the last decade, but the atomic-scale characterization of materials properties and the molecular-scale understanding of photocatalytic processes are still inadequate.

The overall objective of this project is to provide a complete picture of TiO_2 surfaces at the atomic scale, with particular focus on the relationship between atomic structure, electronic properties and (photo-)reactivity in this material. Macroscopic single crystalline surfaces are being studied, where these interrelated aspects can be clearly identified. The PI's are combining extensive and complementary expertise in experimental surface science techniques and first-principles theory applied to this material. As evidenced by a number of well received publications that have been the result of the project so far, this combination has proven a successful approach for obtaining detailed microscopic insights into the surface chemistry of TiO_2.

This project encompasses three, partially interrelated parts:

(1) A characterization of the geometric and electronic structure of the low-index surfaces of various polymorphs (rutile, anatase, and brookite). Work will focus on confirming proposed structural models for rutile (011)-2x1 and on the electronic structure and defects of TiO_2 anatase (101), the most relevant of all TiO_2 polymorphs, with atomically-resolved STM and accompanying DFT calculations.

(2) A detailed study of important adsorbates on TiO_2 surfaces, the resulting electronic structure of the surface/adsorbate systems, and their response to uv-light irradiation. This includes hydrogen (both as an adsorbate and as a bulk impurity); the adsorption of water on anatase (101) and rutile (011)-2x1, in order to obtain complete picture of this most fundamental of all molecules on TiO_2; aromatic molecules (e.g., (chloro-)phenol, one of the most-relevant waste-water contaminants and catechol, an important

intermediate of its decomposition and an anchoring molecule for dye-sensitized solar cells) as well as chloromethanes and –ethylenes, (widespread indoor pollutants and good targets for TiO_2-based photocatalysis).

(3) The 'functionalization' of TiO_2 with noble metal nanoclusters, chromophores, and dopants. Proposed work includes the addition of impurities into the bulk of TiO_2, replacing the cation (e.g., with Fe and V) and/or anion (e.g., with N and F), co-doping effects, an analysis of the resulting effects on the electronic structure, local reactivity, and photo-response.

This broad, yet detailed, program will provide fundamental, mechanistic insight that is essential for real progress towards improving the photoactivity of TiO_2 and related semiconductors.

Harnessing the Chemistry of Carbon Dioxide

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Our research program is broadly focused on activating CO_2 through the use of organic and organometallic based catalysts. Some of our methods have centered on annulation reactions of unsaturated hydrocarbons (and carbonyl substrates) to provide a diverse array of carbocycles and heterocycles. We use a combination of catalyst discovery and optimization in conjunction with classical physical organic chemistry to elucidate the key mechanistic features of the cycloaddition reactions such that the next big advances in catalyst development can be made. We have recently expanded Ni catalyzed cyloaddition to include ketenes, tropones, and cyanamides as efficient substrates. In addition, we have developed a new Fe based catalyst system that converts alkynenitriles and alkynes into pyridines for the first time. Importantly, all reactions proceed under extremely mild conditions (room temperature, atmospheric pressures, and short reaction times), require only catalytic amounts of Ni/L and readily available starting materials, and afford annulated products in excellent yields. Our current focus revolves around understanding the fundamental processes that govern these cycloadditions such that the next big advance in the cyclization chemistry of CO_2 can be made. Concurrent to our annulation chemistry is our investigation of the potential for imidazolylidenes to function as thermally-actuated CO_2 sequestering and delivery agents.

Hydrocarbon Dehydrogenation and Oxidation Over Model Metal Oxide Surfaces

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The research program is directed at understanding structure/function relationships in metal oxide surface chemistry, with a current emphasis on chemistry related to the dehydrogenation of ethane. The chemistry of model Cr_2O_3 and Fe_2O_3 surfaces is being investigated for insight into the surface properties that control selectivity in the reaction of short chain hydrocarbon molecules. Thermal desorption is used to investigate the chemistry of dehydrogenation, coupling (C-C bond formation) and decomposition to surface carbon of selected C1 and C2 fragments formed by the dissociative adsorption of hydrocarbon halides (iodides and chlorides). Synchrotron based photoemission and NEXAFS measurements are used to characterize the surface intermediates.

Cr_2O_3 and Fe_2O_3 are isostructural. Stoichiometric (1012) surfaces provide a simple local site geometry exposing isolated cations with a single coordination vacancy, while the stoichiometric (0001) surface expose cations with multiple (three) coordination vacancies. Previous work with Cr_2O_3 (1012) and (0001) indicates significant structural sensitivity in the surface reaction of C2 alkyl fragments, with a greater propensity to both coupling (C-C bond formation) and surface carbon deposition on the (0001) surface. Fe_2O_3 (1012) is used to provide a change in the electronic properties of the simple, singly coordinated surface cation site (examined previously on Cr_2O_3 (1012)) without a significant change in local coordination or site geometry. The “replacement” of d^3 Cr^{3+} with d^5 Fe^{3+} allows for an almost purely electron change in which the impact of cation 3d electron density can be assessed for the reactions of C1 and C2 hydrocarbon fragments.

Molecular Understanding of Advanced Catalysis for Hydrodeoxygenation

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Transition metal phosphides have emerged as a new class of catalysts for hydroprocessing, which includes hydrodesulfurization (HDS), hydro-denitrogenation (HDN), and hydrodeoxygenation (HDO). An 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. The objectives of the project are listed below.

(1) The synthesis and characterization of catalysts. Transition metal phosphides have been shown to have excellent activity in hydrotreating and are promising for newly emerging biomass treatment processes. A series of compounds (TiP, VP, MoP, WP, Fe_2P, CoP, and Ni_2P) and bimetallics (NiFeP) will be prepared by new methods, and tested with model sulfur and oxygen feedstocks.

(2) Studies of mechanism and reactivity with syngas/H_2O blends. The best catalysts found in the initial tests will be used to study the deoxygenation of ethanol and hydrogenated 2-methylfuran. The former is the simplest of the oxygenated compounds derived from biomass, and the latter is a probe that can react by elimination or substitution. Kinetic studies will be carried out to determine partial pressure dependencies and to give insight on the important steps.

(3) The study of reaction intermediates in HDO by kinetic, spectroscopic, and transient experiments. Adsorbed intermediates will be probed by in situ Fourier transform infrared spectroscopy (FTIR) and the

dynamic behavior of these species will be related to the overall kinetics of the reaction. Understanding of the reaction pathway will lead to identification of difficult steps and the design of improved catalysts.

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

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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 fro the Friedel-Crafts catalysts and that offer the opportunity to develop new technologies that improve the preparation of alkyl and vinyl arenes.

We have identified new cationic Pt(II) catalysts that catalyze the hydroarylation of olefins. Mechanistic studies have resulted in a detailed understanding of the catalyst function, and through variation of the ancillary ligands, we have been mapping structure/activity relationships, which should ultimately allow the rational design of improved catalysts. For example, for one set of catalysts, we have demonstrated that the ancillary ligand donor ability allows systematic variation of the ration of alkyl to vinyl arene.

Also, we have been studying olefin hydroarylation catalyzed by well-defined Ru(II) catalysts of the type TpRu(L)(NCMe)Ar {Tp = hydridotris(pyrazolyl)borate: L = neutral two-electron donors, and Ar = aryl}. These studies have provided information about the impact of variation of the catalyst steric and electronic properties, through variation of the ligand L, on the catalytic reaction as well as competing side reactions. Using these results as a foundation, we have proposed new catalysts that might optimize desirable features. For example, our studies of catalytic hydrophenylation of ethylene and a-olefins by TpRu(L)(NCMe)Ph systems {L = CO, PMe_3, P(N-pyrrolyl)3 or $P(OCH_2)3CEt$} have led us to prepare $TpRu\{P(OCH_2)2(O)CMe\}(NCMe)Ph$. It has been anticipated that this system will possess similar electron density to TpRu(CO)(NCMe)Ph and, as result, provide similar activation barriers as the CO system, which is our most efficient catalyst to date. However, based on our previous studies, we anticipate that TpRu{P(OCH_2)2(O)CMe}(NCMe)Ph will provide enhanced selectivity for linear alkyl arene products for reactions that incorporate a-olefins. This catalyst is currently being studied.

In a new direction, new cationic Ru(II) systems based on poly-pyrazolyl alkane ligands have been studied. The strategy is to use these systems to access catalysts that are less electron rich than TpRu(CO)(NCMe)Ph, a regime that has not yet probed. Preliminary results suggest that such a system does catalyze olefin hydroarylation, and we have been pursuing the development and study of a series of these complexes.

A new Fe(II) catalyst that mediates oxidative olefin hydroarylation has been discovered. This complex activates aromatic C–H bonds at room temperature, and it is selective for the production of vinyl arene, which is a desirable feature. Inexpensive and green oxidants that facilitate catalytic turnover are being sought as well as new ligand motifs that enhance catalyst stability. Success will result in an inexpensive new catalyst.

Observing Carbon-Hydrogen Bond Activation in Chemisorbed Species Using a New Highly Sensitive Optical Method

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The research program in the Yates group is a multifaceted program involving catalysis on metal/oxide systems. In 2011, five papers were published. These papers concern the mechanism of model heterogeneous catalytic reactions where surface science methods have been used, along with theory, to probe the molecular details.

(1) Using STM and ESD, the interaction of CO and O on TiO_2(110) has been investigated. CO-O and CO-O-CO surface complexes have been found. The CO molecules adsorbed near chemisorbed O atoms cause a 70% decrease in O^+ yield in ESD.

(2) The active site for the H_2 + O_2 reaction over a Au/TiO_2 nanoparticle catalyst was located at dual perimeter sites at the interface between Au and TiO_2. An O_2-assisted H_2 dissociation process through a Ti-OOH intermediate was discovered. The activation energy (0.22 eV) was verified theoretically.

(3) Observation of sequential reaction of CO/TiO_2 (first) and CO/Au (second) processes strongly supports a model of an active site located at the perimeter of Au nanoparticles. Theory indicates that a dual site involving Au and Ti atoms causes the activation of the O-O bond, assisted by a neighbor CO. The measured activation energy of 0.16 eV is confirmed theoretically.

(4) An historical account of the quest for the active site in catalysis is given in this general paper for the public.

(5) Using O_2 photodesorption from TiO_2(110) as a method to measure the rate of hole transfer to adsorbed O_2, causing desorption, we have determined that downward band bending is associated with

Au atom adsorption. The Au charge state is approximately +0.2 e/Au atom, and the charge per Au atom decreases with increasing Au cluster size. Theory indicates that the bands bend downward about 0.6 eV upon Au atom adsorption.

Structure and Function of Supported Base Catalysts

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Solid bases are heterogeneous catalysts that have not been broadly exploited compared to solid acids. Solid base catalysts exhibit high activities and selectivities for many kinds of reactions important for fuels and chemicals production, including transesterifications, condensations, alkylations, cyclizations, and isomerizations; however, many of these processes are carried out industrially using liquid bases as catalysts. These applications can require nearly stoichiometric amounts of the liquid base for conversion to the desired product. Replacement of liquid bases with solid base catalysts allows for easier separation from the product as well as possible regeneration and reuse. Basic solids also have the added advantages of being non-corrosive and environmentally-friendly, which allows for easier disposal. However, a molecular-level understanding of solid basicity is required before structure/function properties of new materials can be effectively predicted. Since strong bases are also poisoned by carbon dioxide and water, common side products in catalytic reactions, new base catalysts that are more resistant to deactivation by these molecules need to be developed. The search for novel solid bases that catalyze transformations with high product selectivity, high reaction rate, and low deactivation rate is an ongoing part of this project. In particular, we have recently probed the reactivity of layered double hydroxides for transesterification reactions that are important for conversion of biorenewable resources to fuels and chemicals. The synthesis of biodiesel fuel from plant oils (trigylcerides) and methanol currently employs homogeneous base catalysts to facilitate transesterification although these liquid base catalysts need to be removed and neutralized in the process. The role of water in the transesterification of tributyrin (a model triglyceride) with methanol over the hydroxyl form of hydrotalcite was also explored. Our current work focuses on the coupling of short chain alcohols, such as ethanol conversion to butanol, over solid base catalysts.

Theory Aided Design of Active and Durable Nanoscale Cathode Catalysts

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The goals of this work are to (1) determine the controlling elementary reaction pathways and intrinsic kinetics involved in the oxygen reduction reaction over Pt and Pt based alloys as well as earth-abundant materials and their potential dependent behavior; (2) establish the influence of the extrinsic reaction environment including the surface coverage, alloy composition, solution phase, and electrochemical potential; and (3) understand the mechanisms that control metal dissolution.

Our efforts over this past year have been focused in three major areas: (1) the development of general 3D kinetic Monte Carlo simulation code that can simulate catalysis and electrocatalysis over 3D metal and oxide nanoparticles; (2) the development and application of working 3D kMC code that simulates the detailed mechanisms involved in oxygen reduction reaction over Pt and Pt alloys and integrates in the detailed kinetics that we have established using first principle quantum mechanical calculations over the first 3 years of the program; and (3) the analysis of the novel catalytic materials based on the substitution of Fe and Co ions into nitrogen-containing graphene substrates.

(1) Development of 3D Kinetic Monte Carlo Simulation. We have developed the first general 3D kinetic Monte Carlo simulation code that can construct lowest energy metal nanoparticles and follow the kinetics for any specified reaction system. The user simply specifies the elementary steps and the kinetics in the input file. The code is currently being tested for various different reaction systems, including the oxidation of CO, the oxygen reduction reaction over Pt and Pt alloys, and alcohol oxidation reactions over metals all for fuel cell applications.

(2) Kinetic Simulations of Oxygen Reduction Reaction on Pt and Pt Alloys. We have used a more specific 3D kMC code that we wrote to incorporate the potential dependent reaction energies and activation barriers for the elementary steps that control the oxygen reduction reaction over Pt nanoparticles and Pt-Co surfaces. The resulting turnover frequencies for the formation of water and the desorption of O_2 from simulations over a 1.5 nm Pt cluster have been shown. The simulations clearly show that the reaction at low potentials is limited by the reduction of molecular O_2 to form peroxy intermediates and at higher potentials by the reduction and removal of oxygen from the surfaces. The TOF increases with increasing particle size since the number of 111 facets increases.

(3) Oxygen Reduction over Fe and Co Centers for N-doped Graphene Surfaces. There is currently significant excitement about the development of novel ORR catalysts that are based on N-doped graphene materials that can be synthesized by simply pyrolyzing grapheme in a nitrogen source and adding very small amounts of cheap earth abundant metal acetates to produce active TM-N_4-C site structure. Recent experimental work reveals that TM-N_4-C active site is located between the armchair edges of two graphene sheets that exhibit even higher catalytic activity towards oxygen reduction. Despite these synthetic efforts, there has been very little fundamental understanding of the ORR mechanisms over these TM-N_4-C active centers and the influence of the potential and solvation in the reaction mechanism. We have therefore focused on simulating the complex interfacial solution/Fe and Co—N containing carbon electrode interfaces. First principle density functional theory calculations are currently being carried out to explicitly follow the potential-dependent elementary steps involved in the molecular transformations that proceed at the active catalytic sites at the aqueous/carbon electrode interfaces.

The addition of Fe and Co have shown significant progress in that they can significantly decrease the overpotential losses and allow for ORR to occur quite readily at potentials which mimic those on Pt. We have carried out a full mechanistic analysis of the elementary steps which include the adsorption of oxygen, the initial reduction of O_2 to form the peroxy intermediate, the subsequent dissociation or reduction of the peroxy intermediate to form O*+OH* or HOOH* and the subsequent reduction of these species to form water on the Fe and Co sites as a function of applied potential. An example is the potential dependent reactant and product energies for the initial reduction of O_2 at the Fe site. The results that we have generated indicate that Fe can carry out all of these steps at higher potentials and would be an outstanding replacement for Pt.

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

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The goal of this research program is to provide the basic understanding of surface structure-function relationships needed to develop new and improved catalytic materials involving metal nanoparticles supported on oxide and carbon surfaces for reactions of importance in energy conversion and environmental protection. Our experiments are carefully designed to determine the geometric, energetic and dynamic factors which control the atomic-level structure of certain metal/support interfaces, and the interplay between this structure and the chemical/catalytic reactivity of metal-on-support surfaces.

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. If we are to provide the energy needed for sustained economic development using alternate energy sources (biomass, solar or nuclear) and avoid serious environmental problems, we must develop new and improved solid catalysts, electrocatalysts and photocatalysts for a variety of reactions. This experimental research provides the basic understanding needed to do this. Also, the energy measurements performed in this program (which are unique in the world) will serve as important benchmarks for developing more accurate computational tools for surface science and materials science, which could favorably impact this and many other technologies of importance to DOE.

Recently, we have studied several well-defined model catalysts consisting of metal nanoparticles supported on single-crystalline oxide surfaces, structurally characterized using a variety of ultrahigh vacuum surface science techniques. We have used calorimetry techniques invented here and unique in the world to measure the energies of the metal atoms in these particles and the energy of adsorbed intermediates on these particles, and to determine how these energies depend on the size of the particles and the nature of the oxide support upon which they sit. We have started to see correlations between these energies (which reflect the bonding strengths of these metal nanoparticles to their support and to catalytic intermediates) with each other and with their catalytic properties (sintering kinetics, elementary-step rates and net catalytic reaction rates), specifically how these vary with particle size and the nature of the support surface. We believe that when this correlation is better developed, it will prove crucial to understanding how and why specific structural properties of catalysts determine their catalytic properties. By assessing this interplay between industrially important rates (of sintering and catalytic steps or net reactions) and their thermodynamic driving forces, we expect to provide a deeper fundamental understanding of oxide- and carbon-supported metal catalysts particles. This understanding will facilitate development of better catalyst materials for clean, sustainable energy technologies.

Atomic-Scale Design of a New Class of Alloy Catalysts for Reactors Involving Hydrogen: A Theoretical and Experimental Approach

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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 (DFT) 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.

During the past 3-year period of this project, we have made significant progress on multiple fronts. In particular, we focused our energy on understanding the fundamental reaction mechanism of (1) the water-gas-shift (WGS) reaction and the preferential oxidation of CO in the presence of hydrogen (PROX), both very important reactions for the production and purification of H_2; (2) the production of H_2 from ethanol decomposition; (3) the Fischer-Tropsch synthesis (FTS) of alkane fuels from synthesis gas (CO and H_2 mixtures); and (4) the electrocatalytic oxygen reduction reaction (ORR) and methanol electro-oxidation. In addition, we designed from first-principles, synthesized, and successfully tested with experiments improved catalysts for the WGS, PROX, and ORR reactions. For the next 3 years of our project, we plan on utilizing the framework we have developed for identifying and synthesizing new catalysts for (1) nitric oxide (NO) reduction by H_2, and (2) 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.

POTENTIAL IMPACT

The proposed fundamental research, using a combination of theory and experiments, should have significant impact on designing catalysts at the nanoscale. These new catalysts could greatly facilitate the reduction of nitric oxide to dinitrogen, and the usage of ammonia and dimethyl ether as fuel in direct, low temperature fuel cells, with the former being relevant to environmental pollution remediation and the latter to increasing energy efficiency of power generation in portable applications.

Fundamental Studies of the Reforming of Oxygenated Compounds Over Supported Metal Catalysts

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Our work funded by DOE has involved aqueous-phase reforming of sugars and polyols to produce monofunctional intermediates that serve as precursors to liquid transportation fuels and value-added chemicals. This work has elucidated the factors that control the rate of C-C cleavage to produce H_2 and CO_2, versus the rate of C-O cleavage to produce alkyl moieties. We have elucidated how the performance of a Pt/C catalyst can be altered by the addition of oxo-philic metal promoters, such as Re. The Re-promoter in these catalysts is in a reduced oxidation state; it is located primarily with Pt in the form of nanoparticles, leading to the formation of Pt-Re bonds; and, it leads to stabilization of the metallic nanoparticles against sintering under reaction conditions.

Our work funded by DOE has also addressed the catalytic upgrading to liquid transportation fuels of monofunctional intermediates produced by aqueous-phase reforming of sorbitol and glucose over Pt-Re/C catalysts. We have studied the aldol-condensation of ketones and alcohols to longer-chain hydrocarbons with minimal branching, suitable for diesel fuel applications. This processing strategy is carried out using bi-functional catalysts consisting of basic sites to achieve aldol condensation (e.g., magnesia/alumina, ceria-zirconia) combined with metal sites (e.g., Cu, Pd) to achieve dehydrogenation of alcohols and hydrogenation of C=C double bonds in dehydrated aldol-adducts. In addition, we have studied bi-molecular reactions of carboxylic acids to form higher molecular weight ketones along with the formation of stoichiometric CO_2 and H_2O.

Our current work deals with fundamental catalytic issues associated with the use of levulinic acid and gamma-valerolactone (GVL) as platform molecules for the conversion of renewable biomass resources to fuels and chemicals. We are studying the catalytic coupling between levulinic and formic acids to form GVL in aqueous solutions in the presence of sulfuric acid.

The results from this work will advance understanding of the factors controlling the reactivity of highly oxygenated biomass-derived reactants (e.g., levulinic acid and esters) on supported metal catalysts, thereby advancing the ability to develop new catalytic processes for the conversion of renewable biomass resources to valuable fuels and chemicals. An important outcome from this work will be the elucidation of catalysts and catalytic reaction conditions for the conversion of ligno-cellulosic biomass to hydrocarbons with molecular weights suitable for use as transportation fuels.

Mechanisms of Organometallic Aerobic Oxidation Reactions Catalyzed by Copper

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Advances in catalysis are needed to address many of the major challenges facing our nation and world, and reduction of our dependence on precious-metal catalysts for energy-related applications and chemical synthesis is an important goal of catalysis research. The development of new catalytic processes that employ base metals (typically, first-row transition metals) will benefit significantly from a more sophisticated understanding of their fundamental reactivity patterns. This project is directed toward the mechanistic characterization and development of copper-catalyzed aerobic oxidation reactions, specifically, oxidative coupling reactions that form carbon-heteroatom bonds. Insights from these studies should provide a basis for the replacement of palladium and other noble metals in aerobic oxidation and carbon-heteroatom coupling reactions.

This project has two main components: (1) kinetic and mechanistic characterization of Cu- catalyzed aerobic oxidation reactions, specifically, the oxidative heterofunctionalization of aryl- and vinylboronic acids and alkynes, and (2) investigation of the fundamental organometallic chemistry of copper in oxidation states higher than +1, that is, organocopper(II) and -copper(III) complexes.

These two efforts are highly complementary. Insights gained from our mechanistic studies of catalytic reactions have already highlighted the role of organometallic intermediates and transformations that have little or no precedent; and the characterization of the fundamental organometallic chemistry of Cu will contribute to an improved understanding of key steps in catalytic reactions. Both of these efforts are playing an important role in the expansion and development of new Cu-catalyzed aerobic oxidation reactions, a prospect that has already been realized in the early stages of this project. Long term, we anticipate this work will lead to general strategies for selective aerobic oxidative functionalization of organic molecules, including C–H bonds.

Metal-Metal Bonded Reaction Intermediates in C-H Functionalization

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Funding:	$155,000

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 M2(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.

Within area one, we have discovered a new, single-electron transfer mechanism that is operable in C–H amination catalyzed by some dirhodium catalysts. We have also observed new, metastable intermediate species upon reaction of dirhodium complexes with organic diazo compounds and are currently employing several spectroscopic methods (NMR spectroscopy, resonance Raman spectroscopy, and X-ray absorption spectroscopy), in attempt to identify this novel species. In area two, we have characterized an unprecedented intramolecular aryl C–H amination reaction involving a nitrido compound that occurs under surprisingly mild conditions. We used variable temperature kinetic measurements to determine activation parameters and the kinetic isotope effect of aryl C–H functionalization, and we determined the overall reaction enthalpy via calorimetric techniques. These experimental benchmarks were used to calibrate DFT calculations of the reaction coordinate pathway, with the result that C–H amination occurs via an electrophilic aromatic substitution mechanism. Recently, we have used a new ligand design to disfavor intramolecular C–H amination to promote intermolecular C–H amination, and we are finishing up a study on direct conversion of benzene to aniline. Currently, this reaction is stoichiometric, and further work in this area will be focused on developing a catalytic reaction. In addition to these studies, we have published a major article that seeks to explain the exceptional catalytic reactivity of metal-metal multiply bonded compounds in C–H functionalization catalysis. The premise of this work is that three-center/four-electron bonds within a M=M=E framework (here, E = carbene, nitrene, or nitride) lead to superelectrophilic reactivity.

Atomic Resolution Imaging and Quantification of Chemical Functionality of Surfaces

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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 chemically well-defined tips, chemical interactions can be precisely quantified and assigned to exact positions within the lattice. To further improve on imaging robustness, we are pursuing, as an integral part of this proposal, several routes for instrumental and methodological upgrades, which include new faster probe sensors and modified data acquisition procedures.

During the FY 2011 reporting period, we completed the work on the oxygen/copper (100) Cu_3O_2 surface phase, which we chose as a catalytic model material during the initial reporting period due to its unique structural and chemical characteristics. In particular, the combination of distinct symmetries of Cu and O atoms, the abundance of well-defined defects, and the simultaneous recording of the tunneling current allowed achievement of major improvements. These improvements included better electronic setup and data analysis procedures that permit considerably faster data acquisition while providing more stable imaging with better resolution in two complementary data channels (force and current).

A detailed analysis showed that with a metal-terminated tip, oxygen atoms are revealed in the force channel while copper atoms appear bright in the tunneling current. From these and other measurements, the following conclusions could be drawn:

(1) Defects that affect only copper atoms are invisible in the force channel if measured with a well-defined metal-terminated tip, but appear in the tunneling current channel. This demonstrates that chemically selective information can be provided by the two data channels if tip termination is appropriately chosen.

(2) Even though the oxygen-sensitive force images do not directly reveal the presence of the defects that are solely due to a rearrangement of copper atoms, their effect on the surrounding oxygen atoms manifests itself as significant variations in the forces between individual atoms, with oxygen atoms adjacent to the defects typically showing enhanced interactions with the metal atom at the tip apex. This suggests that defects are nucleation sites for metal growth, affecting everything from epitaxial growth to how metal particles, such as catalyst particles, can be anchored onto oxide supports.

(3) Other data sets that have likely been obtained with oxygen-terminated tips, as they emphasize the positions of copper atoms in both force and current channels, show enhanced interactions at 90° domain boundaries, implicating these sites as active for initiating bulk oxidation.

Once work on the Cu_3O_2 surface phase was completed, we switched to TiO_2 due to its greater importance as a model catalyst. On this material, we were also able achieve high-quality, combined NC-AFM and scanning tunneling microscopy (STM) imaging and to record 3D data sets of surface regions including defects. Due to the recent nature of these results, analysis is still in progress.

Bifunctional Ligands for Enhanced Selectivity in Organometallic Catalysis

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We are looking for general strategies for endowing first row d metals as well as inexpensive second and third row Mo and W and even perhaps Main Group elements with the same high activity we now see for Pt metals. We expect a very big cost advantage in moving from our usual Ir ($16,800/lb) to Co ($40/lb). To do this we are replacing the usual OA/RE catalytic cycles with mechanisms that involve proton/hydride donation from the catalyst to the substrate. Since no change in oxidation state is involved, we expect this to open the way to using inexpensive d metals and maybe even main group elements in the proposed catalysts. The target reaction is 'hydrogen borrowing' and related hydrogen transfer reactions. Some of our prior catalysts have proved useful in industrial synthesis but these mainly relied on Ir, a rare metal. With the increasing prices of platinum group metals, the cost advantage of base metals, already big, is likely to increase even further. The catalysts that we make sometimes also prove useful for other DOE projects, both in our own lab and elsewhere. The project also benefits from a longstanding computational collaboration with Odile Eisenstein (Montpellier, France).

Structured Carbon Supports for Aqueous PhaseReforming and Fuel Cell Catalysts

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Funding:	$160,000

The goal is to develop the fundamental science of nanoparticles of oxides covalently bonded to carbon nanotubes (CNT), with specific reference to ZrO_2 and sulfated ZrO_2, and to develop methods of directing the deposit of metals, e.g., Pt, on the oxide and/or the multi-walled CNT (MWCNT) support of the ZrO_2/MWCNT composite. This study will suggest directions for the synthesis and characterization of other nano-oxide CNT composites. As progress for the current grant year, we report on the synthesis and characterization of colvalently bonded ZrO_2 nano particles on MWCNT. We also report on completion of the design of catalysts for single wall CNT (SWCNT) synthesis (a theme of prior DOE grant) and initial work on developing methods to selectively deposit Pt on ZrO_2 or MWCNT components of ZrO_2/MWCNT composite support. The grant objective is of relevance to the DOE mission because renewable energy sources of the future will require catalysts to produce fuels from biomass, and the need for catalysts that have solid acid and hydrogenation catalytic activity in aqueous media for this purpose.

This project proposes to investigate the fundamental science of catalysts for conversion of biomass to hydrogen and for producing useful power from alcohols in fuel cells. The extraction of hydrogen is accomplished in water from soluble, biomass derived, oxygenated hydrocarbons by aqueous phase reforming (APR, the catalytic, high pressure reaction between water and oxygenated hydrocarbons to produce hydrogen and carbon dioxide). The direct alcohol fuel cell electrodes require catalysts for the oxidation of alcohol. Catalysts for APR and direct alcohol fuel cells use catalysts which have the active component dispersed on a support, a high area material that stabilizes small metal particles of metal, such as Pt. Carbon supports are advantageous for APR because they are stable in the aqueous phase (do not dissolve as common oxide supports do) and are advantageous for catalysts used in fuel cells because of the necessary electrical conductivity.

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

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Funding:	$155,000

Transition metal oxides play key roles in a wide range of processes central to efficient utilization of scarce resources with minimal environmental impact. Our goal has been to determine the relative importance of geometric and electronic effects in determining the reactivity of these catalysts by creating well-defined surfaces where the electron density and local structural environment can be varied independently. Recently, we have focused on the complementary areas of creating and characterizing the structure and reactivity of oxide heterostructures in which the influences of structural and chemical effects in supported oxides are distinguished; and on characterizing the surface structure and chemistry of prototypical oxide structures in which the cations can be varied without changing the structural environment of the active cation.

In the latter area we have investigated prototypical scheelite-, spinel-, and perovskite-structured catalytic materials using a range of surface science methods including electron diffraction, scanning tunneling microscopy, photoelectron spectroscopy, molecular beam epitaxial growth (MBE), ion scattering, and thermal desorption. We have characterized the non-polar (100) surface of $CaWO_4$, the base member of the scheelite class of materials which includes many important oxidation catalysts. We found that $CaWO_4$ behaves vastly differently from WO_3, which we have extensively studied; unlike WO_3, $CaWO_4$4 is extremely difficult to reduce, and alcohols that readily dehydrate on WO_3 only physisorb on $CaWO_4$ (100). Ion scattering results indicated that the coordinatively unsaturated W sites that strongly adsorb alcohols on WO_3 are not accessible on the $CaWO_4$ (100) surface. We used adsorption of the Lewis acid BF_3 to characterize the basicity of surface oxygens on the $CaWO_4$ surface; although Ca is considered to impart basic character, there was no evidence of strong basic sites on the $CaWO_4$ surface. The results highlight the difficulty in predicting the behavior of complex oxides based on the behavior of the simpler constituent oxides.

For the perovskites we have investigated $LaCoO_3$ (100) and (110) surfaces. This material was chosen as prototypical perovskite because of the distinct functionality of Co as a redox center and La as a basic oxide, the interesting properties of this material as both a catalyst support and active phase, and because of fundamental interest in modifications of polar perovskite surfaces that can influence structure and reactivity. Regarding the latter, in contrast to our prior findings for $LaAlO_3$, we found no evidence of reconstructions of the polar $LaCoO_3$ surfaces. Photoelectron spectroscopy data indicate that the material is metallic and so we suggest that the polar surfaces are compensated by redistribution of the conduction electrons rather than atomic rearrangements as in insulating $LaAlO_3$. We have characterized the reactivity of the $LaCoO_3$(100) surface using alcohol thermal desorption which thus far shown mostly molecular desorption. As the (100) surface may terminate in either LaO or CoO_2, we are investigating the role of the surface termination in determining the reactivity.

We have studied Co_3O_4 and orthovanadates of the form $M_3V_2O_8$ as examples of spinel- structured catalytic oxides (the latter is a cation-deficient spinel). The former has recently attracted attention because of the observation of low temperature CO oxidation and NO reduction activity, while the latter are candidate oxidative dehydrogenation catalysts. In the orthovanadates, M can be divalent cations including Mg, Ni and Co. This group of materials forms a bridge to our prior work on epitaxial vanadia catalysts where the interface with the support affects the structure and reactivity of the vanadium cations as opposed to vanadium ions in a well-defined crystal structure where the secondary cation can be varied without changing the structure. For Co_3O_4,we have found interesting changes in the termination of (110)-oriented epitaxially grown thin films depending on the environment, as well as an interaction with Al_2O_3(0001) that enables the formation of thin Co_2O_3, a material that is not otherwise stable. Meanwhile, we have characterized the structural, electronic, and chemical properties of stoichiometric $Ni_3V_2O_8$ (010) surfaces. We find that the surface terminates in an unreconstructed spinel “A” plane that exposes both Ni and V cations. It is an insulator that only weakly adsorbs 1-propanol. We are currently investigating the effect of oxidation and reduction on the reactivity of this surface. Moving forward, we plan on investigating Co orthovanadate which will offer an interesting comparison to our parallel efforts on $LaCoO_3$ and Co_3O_4.

DOE National Laboratories

Chemical Energy (Homogeneous and Interfacial Catalysis in 3-D Controlled Environments)	
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Funding:	$1,320,000

The rapidly increasing global energy demand has led to an intensive search for secure and sustainable sources of clean energy. Catalysis plays a crucial role in enabling and controlling the chemical conversion of a variety of feedstocks to renewable fuels and energy. The overarching goal of this research is to develop a fundamental understanding of homogeneous and heterogeneous catalytic transformations.

Our collaborative research effort is geared toward developing and characterizing multifunctionalized mesoporous materials that integrate the selectivity of 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, well-characterized heterogeneous catalysts is being examined in several classes of chemical reactions, including enantioselective hydrogenation, hydroamination, bond activation, polymerization and oxidation. Current research also includes the development of catalytic systems that combine biological and thermo- or photochemical catalysis into a "one pot" cascade. The 3D catalytic materials are examined using a variety of chemical, physical and theoretical methods, highlighted by new solid-state NMR 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 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.

Development of Homogeneous Catalysts for Water Oxidation and Proton Reduction-Applications Toward Photochemical Energy Storage

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Funding:	$400,000

This project entails a comprehensive research effort focused on the design and discovery of homogeneous catalysts for the oxidation of water and for the selective reduction of protons and small molecule substrates, two processes that must ultimately be coupled to achieve the efficient conversion of solar energy into chemical fuels. Once these catalysts are synthesized, they can be coupled to framework structures containing arrays of light-harvesting components, thus creating catalysts suitable for use in fuel generation processes that are electrochemically or photochemically driven.

Institute for Catalysis in Energy Processes

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Funding:	$900,000

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 the catalytic oxidation of small alkanes (e.g., methane and ethane) and on the photocatalytic reduction of carbon oxides (e.g., CO_2). The Argonne portion of ICEP comprises activities in (1) understanding photocatalytic reactions catalyzed by TiO_2, (2) the synthesis and molecular characterization of supported oxide catalysts used for alkane oxidation, and (3) the synthesis, characterization, and evaluation of homogeneous catalysts for alkane conversion.

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. 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 that is linked to the EPR experiments, the key reaction steps have been identified and analyzed. This work lays the foundation for better understanding photocatalysis and the design of more effective processes.

New synthesis methods for the formation of catalytic oxide monolayers have been explored using atomic layer deposition (ALD) and organometallic grafting. These methods have led to the exquisite control of surface vanadium oxide species that are highly active for alkane activation. The molecular identification of these species has been accomplished for the first time using advanced resonance Raman spectroscopy and associated computational studies. New molecular forms of surface vanadium oxide were detected and their chemical properties for hydrogen reduction were established.

The homogeneous catalysis group at Argonne is exploring the use of modular, flexible, and tailorable nature of covalent porous organic polymers (POPs) functionalized with well-defined single-site catalytic centers to develop materials possessing reactivity-defining microenvironments. Such materials can then be deployed as catalysts for the activation of strong bonds (C-O, C-H, O-O, O-H), via the deliverance of oxidizing or reducing equivalents within a thermally stable solid.

Structure Composition Function Relationship in Supported Nanoscale Catalysts for Oxidation Hydrogen Cellulose

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Funding:	$400,000

The objective of this research program is improved fundamental understanding of composition/structure/function relationships in supported heterogeneous catalysts for reactions that oxidatively convert cellulose to monosaccharide sugars such as glucose and other chemical intermediates. In homogeneous catalysis, control of the redox chemistry governing catalysis is accomplished by changing the type of organic ligands attached to the central metal. Heterogeneous catalysis, while sometimes more difficult to control, affords greater latitude to control the physical and chemical nature of the metal clusters. By exploiting the ability to size-select specific metal clusters or alloys along with the type of support material, we can control the redox chemistry of the catalyst for specific reactions. The fundamental understanding that will result from these studies will provide insight into controlled oxidation of large biomolecules containing multiple –OH bonds.

Structure/Composition/Function Relationship in Supported Nanoscale Catalysts for Hydrogen

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Funding: $730,000

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. One specific goal has been to determine if the catalytic activity for hydrogen production from methanol can be significantly improved by preparing catalysts that only partially adsorb CO under reaction conditions. The catalysts are supported metal, alloy, carbide, and nitride nanoparticles and clusters with an emphasis on supported catalytic clusters in the size range <1 nm, i.e., ~2-50 atoms. The proposed research integrates efforts in (1) the synthesis and stabilization of uniform, supported clusters and oxide promoters; (2) the characterization of cluster size, atomic structure, stability, and electronic structure during synthesis, pretreatment, and catalytic reaction; (3) the investigation of catalytic and chemical events on the clusters that are relevant to hydrogen production; and (4) the computational quantum chemical modeling to understand and predict experimental results.

A major outcome from the research has been the development of atomic layer deposition (ALD) as a method for controlled catalyst synthesis. The ALD methodology has been advanced to provide for the synthesis of ultra-uniform, ultra-small supported metal and metal alloy particles. ALD has also been used to synthesize the oxide layers that serve as the supports for the catalytic nanoparticles. ALD has enabled a new design tool for catalyst synthesis by providing the means to form porous oxide capping structures over the metal nanoparticles. These capping structures prevent particle coarsening that leads to catalyst deactivation. As a result advanced catalysts with exceptionally long lifetimes have been achieved.

Catalysis on the Nanoscale: Preparation, Characterization and Reactivity of Metal-Based Nanostructures

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Funding: $550,000

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. Studies focus on model nanocatalysts to develop principles applicable to the improvement of catalysts for energy conversion processes, particularly in fuel synthesis and use. The Nanocluster preparation techniques include soft-landing of size-selected clusters and reactive layer deposition; and these have been used to investigate the activity of novel transition metal carbide, oxide, and sulfide nanocatalysts for desulfurization, hydrogen production, and oxygenate synthesis. The model systems also include “inverse” nanocatalysts of metal oxide clusters deposited on metal supports which exhibit unique electronic, morphological and reactivity properties. Theoretical modeling using DFT is an integral part of this program and is used to explore the role of light atoms (C, S, P) in modifying the activity of metal compounds, the influence of cluster-support interactions on reactivity, and the identification of key intermediates and reaction steps in complex surface reactions. Two growing areas of research are in oxygenate synthesis and use. One is in C1-C4 oxygenate synthesis via CO/CO_2 hydrogenation using oxide-supported metal, metal oxide and metal sulfide nanoclusters. The other makes use of a new instrument with capabilities for UHV surface science, cluster deposition, and characterization of model nanocatalysts under electrochemical conditions, with a focus on oxygenate fuel cell electro-oxidation reactions.

Catalysis: Reactivity and Structure

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Funding:	$1,143,000

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. At the present time, we are engaged in fundamental studies examining the behavior of catalysts used for the production of clean fuels and the prevention of environmental pollution. 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 several coordinated approaches. First, powder diffraction and x-ray absorption studies of "real-world" systems enable in-situ time-resolved studies of the formation and transformations of supported metal clusters and metal oxides and carbides under catalytic reaction conditions. These are carried out using our x-ray diffraction facilities at beamline X7B and facilities for X-ray absorption spectroscopies at beamlines X18B and X19A. The program is also developing new approaches for the in-situ characterization of heterogeneous catalysts and is actively involved in the operation of the Synchrotron Catalysis Consortium (SCC). Second, ultra-high-vacuum surface science investigations of well-defined model systems are pursued to understand basic principles of surface reactivity and its control by surface modification, and to identify active sites and characterize their electronic and structural properties. X-ray photoemission and absorption spectroscopies at the U7A beamline at the National Synchrotron Light Source (NSLS) are essential to this part of the work. Third, quantum-chemical calculations based on density-functional theory are performed to help in interpretation of experimental results and to study basic aspects of catalytic reactions.

Mechanisms for Water Gas Shift Reaction

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Funding: $650,000

We address fundamental issues in the mechanisms for the water-gas shift reaction through an integrated experimental and theoretical research program. The water-gas shift reaction (WGS: $CO + H_2O$ reacts to $H_2 + CO_2$) is a critical process for providing pure hydrogen for fuel cells and other applications. Improved air-tolerant, cost-effective WGS catalysts for lower temperature processing are needed. Ceria-, titania- and molybdena-based catalysts are expected to be the next generation of WGS catalysts for industrial applications. The design and optimization of these WGS catalysts depends on a better understanding of their structure and function. We are following a coordinated research program to understand the active sites and reaction mechanisms 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 structure and mechanism in this important process.

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

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Funding: $720,000

This project studies basic problems of electrocatalysis to establish principles for the improvement of fuel cell electrocatalyst function, durability and cost. The focus is on platinum monolayer electrocatalysts, based on core-shell nanoparticles with platinum shells, for the O_2 reduction reaction (ORR); and ternary and bimetallic electrocatalysts for ethanol and methanol oxidation to CO_2. Studies using well-defined single crystal surfaces are 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 obtain deeper insight into the kinetics of the O_2 reduction reaction, the role of proton transfer, and the effects of surface bonding of O_2, O, and OH to develop nanostructured catalysts with high activity. We investigate the durability of core-shell nanoparticles, and are exploring a new mechanism - core protection of the shell - that contributes to substantial improvements in stability compared to standard Pt nanoparticle catalysts. We are also studying hollow nanoparticle catalysts and a second generation of core-shell nanoparticles based on the stabilization of cores by alloying or by the placement of subsurface metal monolayers. The goal of our work is to contribute to resolving major challenges in existing fuel cell technology related to the limitations of electrocatalysts for the O_2 reduction reaction, and thereby enabling its successful commercialization. We have also recently expanded studies of ternary catalysts for ethanol oxidation and are pursuing a new discovery of pronounced increases of catalytic activity of Pt for ethanol and methanol oxidation caused by support-induced tensile strain.

Ultrafast and Chemically-Specific Microscopy for Atomic-Scale Imaging of Nanophotocatalysis

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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$420,000

This project is developing new approaches to study photocatalytic reactions at the surfaces of solids, which are important in processes such as solar energy conversion to fuels and in photocatalytic environmental remediation. Understanding such photocatalytic chemical transformations, which are often carried out on surfaces with heterogeneous nanoparticle structures, poses experimental challenges due to the complex relationship between light-stimulated hot charge carriers and the chemical reactivity. We are addressing these challenges by developing new techniques that combine spectroscopic chemical specificity, sub-nanometer spatial resolution and sub-picosecond temporal resolution. Photoinduced chemical transformations are studied on nanostructures and model catalyst surfaces in two ways: (1) by mapping light-induced electronic excitations and the chemical reactions they drive with new femtosecond-laser-based techniques capable of probing the population of excited electronic states with near-atomic spatial resolution and ultrafast temporal resolution and (2) by investigating non-thermal, electron-mediated transformations and reactions on photocatalyst surfaces with atomic precision and chemical specificity, using laser excitation or the scanning tunneling microscope to inject carriers into surface supported atoms and molecules. The multidimensional approach underlying this work represents a new way of imaging surface chemical reactions and their relation to ultrafast carrier dynamics.

Nanoscience & Nanoparticles for 100% Selective Catalytic Reactions

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Students: 4 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $800,000

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. There are three main areas of emphasis that are combined in this program: (1) fabricate 3-dimensional or 2-dimensional catalyst systems with complete control of catalyst nanoparticle 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 (4) 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.

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

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Students: 5 Postdoctoral Fellow(s), 7 Graduate(s), 0 Undergraduate(s)
Funding: $2,030,000

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 pursue independent research goals while extensively collaborating via joint supervision of graduate students and postdoctoral associates, and by extensively sharing instrumentation.

Fundamentals of Heterogeneous Catalysis on Surfaces and Nanostructures

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Students:	4 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$1,660,000

The overarching goal of this proposal is to understand the fundamental relations between the atomic and nanoscale structure of catalysts and their catalytic properties. The approach is to use an array of experimental techniques, supplemented by computational studies, to explore structure, structural evolution, chemisorption, surface chemistry and catalytic reaction on model catalysts. Both single crystal surfaces and specially synthesized high surface area nano materials are used as model systems. New synthetic methods are explored to prepare new materials with selected or unusual properties. Of particular interest are model catalyst systems based upon active, reducible oxides such as CeO_2 or Co_3O_4, and upon Au or alloyed Au nanoparticles on a variety of oxide and phosphate supports. We seek to understand how organic oxygenates molecules adsorb and react on CeO_2 and how this interaction is guided by the surface structure of the CeO_2 and the ability of the oxide to contribute oxygen during oxidation reactions. We also seek to understand the factors that control the activity and stability of Au in alloyed Au nanoparticles and the reaction pathways for oxidation reactions in supported Au catalysts. The use of dumbbell structures, surface modified supports and alloying components are used to learn how to increase stability and modify activity in the Au catalysts. Success in this program will create new approaches for preparation and implementation of active and selective catalysts that could be directly related to fuel cells, batteries, pollution control, hydrogen generation and utilization, combustion, bio-fuel production, and chemical synthesis.

Organic Chemical Transformations at Interfaces

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,100,000

The overall goal of this program is to gain a comprehensive understanding of the structure-reactivity relationships that control the kinetics and mechanisms of thermochemical transformations for oxygen-containing organic molecules in the gas phase, in solution, and at solid metal oxide interfaces. The focus is on unraveling the free-radical reaction pathways involved in the thermochemical transformations of oxygenated organic molecules that are models for structural moieties present in biomass, which are less well understood than their hydrocarbon counterparts. This fundamental research seeks to provide new understanding in three specific areas, namely (1) the influence of oxygen functional groups on the kinetics and reaction pathways involved in the thermochemical transformations of lignin model compounds, (2) the impact of surface interactions and pore confinement in mesoporous metal oxides on organic free-radical transformations including the role of surface hydrogen bonding of oxygen functional groups, and (3) the influence of local nanostructure of the interfacial environment on molecular dynamics and chemical transformations. An integrated approach is employed that involves (1) the synthesis of target organic molecules, ordered mesoporous metal oxides, and pore-derivatized hybrid materials; (2) the determination of pyrolysis reaction rates, mechanisms, and product selectivities; (3) advanced solid-state NMR (e.g., O-17) and quasi-elastic neutron scattering studies of the structure and dynamics of the organic-inorganic interface; and (4) theoretical and molecular modeling/dynamics studies to analyze in detail organic free-radical reaction pathways and to probe structure and dynamics of the organic-inorganic interface. The fundamental knowledge gained from these studies will not only contribute broadly to scientific fields such as catalysis and nanostructured materials, but will also contribute to the development of improved technologies for the utilization of renewable resources such as biomass as a sustainable source of transportation fuels and chemical feedstocks.

Understanding Ligand Protected Metal Nanoparticles for Catalysis

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Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$50,000

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) discover 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."

Chemical Transformations at Complex Interfaces

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Students:	15 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$4,176,000

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 six 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, (4) a modular energy based approach to molecular catalyst design, (5) IIC Operations, and (6) fundamental studies of CO_2 conversion.

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

The NHxBHx series of compounds will be the focus of the research. While these materials provide favorable volumetric and gravimetric densities (e.g., 245, 196, 140, 75 gm H_2/kg for x from four to one), little is known about how these materials release hydrogen from the solid state and what factors control the reactivity and selectivity of product distribution. The proposed research will use a synergistic combination of experiment and theory to develop a fundamental understanding of the key chemical and physical properties that control the thermochemistry and kinetics of the molecular processes related to hydrogen release and uptake. The effects resulting from nanoscaling of hydrogen-rich materials and interfacial interactions will be explored. This research will result in knowledge that will lead to the development of new materials that release and absorb hydrogen at moderate temperatures and pressures. In consequence, the proposed work specifically addresses the focus area "Novel Materials for Hydrogen Storage" and peripherally the "Design of Catalysts at the Nanoscale" of the HFI call. These fundamental studies will provide a strong basis for support of DOE's Centers of Excellence and develop new theoretical and experimental tools to investigate hydrogen-rich materials.

Early Career - Catalyst Biomimics: A Novel Approach in Catalyst Design

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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$500,000

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

New Bio Inspired Molecular Catalysts for Hydrogen Oxidation and Hydrogen Production

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Funding:	$620,000

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. Our objective is to design and synthesize biologically inspired functional models that catalyze the oxidation and production of hydrogen with high activity and low overpotentials. Our focus has been on inexpensive, earth-abundant metals, such as nickel, cobalt, and manganese, using ligands with pendant amines that accelerate catalysis through the hydrogen bonding interactions. Nickel complexes with pendant amines ligands catalyze the oxidation of hydrogen and the production of hydrogen from reduction of protons, and cobalt catalysts have been discovered for hydrogen production. A manganese complex was found to give heterolytic cleavage of hydrogen, with the hydride being transferred to the metal and the proton being located on nitrogen. We propose new studies in which changes in the first and second coordination spheres will be used to achieve optimal properties for H_2 binding, heterolytic cleavage of H_2, proton-coupled electron transfer reactions, and catalysis of the oxidation and production of H_2.

Center for Interface Science and Catalysis	
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Students:	2 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$2,000,000

The SUNCAT Center for Interface Science and Catalysis was formed in June of 2010 to study the electronic and structural factors determining the catalytic properties of solid surfaces as a basis for the design of new catalysts. In 2011 progress can be summarized as follows:

METHOD DEVELOPMENT

Work has been performed to develop new exchange-correlation functionals that can describe both strong and weak chemical bonds and at the same time provide an estimate of the errors one can expect. A web application has been developed for looking up calculated reaction and activation energies for elementary coupling reactions occurring on metal surfaces.

THEORY OF SURFACE REACTIVITY

By performing a large series of density functional theory calculations of reaction energies and activation energies of a large number of elementary reactions on a number of metal and oxide surfaces, general scaling relations have been derived between activation and reaction energies and between reaction energies scale and adsorption energies of the atoms bonding to the surface. This forms the theoretical basis for understanding trends in surface reactivity. The work also provides a systematic reactivity database which can be accessed using the web application. The database consists of reaction and activation energies for all reactions involving C-C, C-H, C-O, O-O, O-H, N-N, C-N, O-N, N-H splitting/formation for molecules with up to three C, N, or O atoms on a number of different facets and steps of 15 transition metals. Work is underway to understand electronic factors determining these trends. Other work is aimed at understanding finite size effects in the reactivity of Au and Pt clusters by performing calculations of adsorption energies of clusters with up to 1500 atoms (3.7 nm diameter). Simulations to understanding ps dynamics of CO on Ru surfaces observed in LCLS experiments are underway.

APPLICATIONS TO SURFACE CATALYTIC PROCESSES

For syngas reactions, the scaling relations have been used to reduce the number of independent variables characterizing a surface. For the case of methanol synthesis, it turns out that the C and the O are adsorption energies. This means, that we can calculate the variations in the methanol synthesis rate as a function of these variables. Once the descriptors of the activity have been identified (the C and O adsorption energies for methanol synthesis) it is simple to screen a number of alloys as potential catalysts (if they can be made and are stable). Several have been identified as potential new catalysts and have been tested in collaboration with experimental groups.

Condensed Phase and Interfacial Molecular Science

Institutions Receiving Grants

Generation, Detection and Characterization of Gas-Phase Transition Metal Containing Molecules

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Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding:	$114,000

There is considerable interest in using gas-phase transition metal dioxides, such as titanium dioxide, TiO_2, as models understanding the catalytic activity of extended systems such as rutile. We have recently demonstrated that these model systems can indeed be generated in the gas-phase and characterized by high-resolution laser spectroscopy. Specifically, we have been able to determine bond lengths, bond angles, and permanent electric dipole moments for metal dioxides. We recorded and analyzed for example, the A-X band system of TiO_2 generated in a supersonic expansion of laser ablated titanium with an Ar/O_2 mixture. Our experience with TiO_2 has identified the experimental conditions necessary for efficient production and detection of metal dioxides while at same time suppressing the production and detection of monoxides. We have recorded the low-resolution laser induced fluorescence (LIF) spectra of molecules generated in the reaction of ablated zirconium (Zr), hafnium (Hf) and nickel (Ni) with an Ar/O_2 mixture and have tentatively assigned the observed spectra to ZrO_2, HfO_2 and NiO_2. The mass selected, resonance enhance multi-phonon ionization (MS-REMPI) spectrum has also been recorded in collaboration with Professor John Maier at the University of Basel. Like TiO_2, the ground state of ZrO_2 has a large apex angle (108.1º). The observed excitation transitions wavenumbers were fit to determine the force constants using a normal coordinate analysis. A comparison of the excitation spectrum for ZrO_2 with that for TiO_2 reveals that strong progressions in the non-symmetric mode (e.g., are present in ZrO_2 but absent in TiO_2. Evidently, vibronic coupling is much larger in the excited state of ZrO_2 than TiO_2.

Single-Molecule Interfacial Electron Transfer

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Funding:	$188,000

Our research 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.

Electronic Structure of Transition Metal Clusters and Actinide Complexes

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Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$121,000

Noble metal quantum clusters (QCs) are fascinating materials of intense research today in the fields of chemistry and nanoparticles. Our research during FY 2011 continued to focus on QCs, showing confinement in their absorption profiles. Thus in a joint experimental computational study, we reported two luminescent molecular quantum clusters of silver, $Ag_7(H_2MSA)_7$ and $Ag_8(H_2MSA)_8$. Global optimizations and property calculations are performed in the framework of density-functional theory (DFT-PBE) to search for the leading candidates with the lowest-energy. The simulated excitation spectra of these two clusters are in good agreement with the corresponding experimental spectra. The presence of –RS-Ag-RS- as a stable motif has also been confirmed in all of the lowest energy structures. Our computed vibrational spectra are also consistent with experimental findings. The results of these studies have been published in a recent paper in JPC A.

In yet another exciting Angew Chem paper that is recently accepted, we have reported the results of an alloy cluster containing a 13 atom core, with a composition, $Ag_7Au_6(H_2MSA)_{10}$ (H_2MSA = mercaptosuccinic acid) was synthesized from silver clusters via a galvanic exchange reaction. The clusters were characterized by diverse spectroscopic and microscopic tools as well as by elemental analyses. Electrospray ionization mass spectrometry gives distinct features for the cluster. The alloy cluster shows luminescence with a quantum yield of 3.5% at room temperature, several times higher than the parent clusters, allowing its luminescence images to be photographed. Synthetic conditions were optimized and the ligand cover of the cluster was modified with various alkyl/aryl thiols. Solvent and ligand dependent luminescence and lifetime of the cluster were studied. This alloy cluster points to the diverse category of materials which may be useful in catalytic and photophysical applications. Theoretical calculations for $(Ag_7Au_6)SCH_3)_{10}$ suggest a distorted icosahedral core. Our most recent work focused on the electronic structures and spectra of $Ag_9(SCH_3)_7$ clusters and 25-atom silver and gold clusters. We are also working on actinide complexes with various environmentally interesting ligands.

Early Career - Ultrafast Electron Transport Across Nanogaps in Nanowire Circuits

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

How does an electron move from one end of the molecule to the other end? Which orbitals do participate in this electron transport process? Which molecular motions are involved? How fast is this process and how does it depend on the molecular structure? What is the repeatability of this process? How can this process be improved by making use of smart chemistry? Such questions are of direct relevance to the field of molecular electronics, where single molecular components are used to move charges from one contact to the next. A precise understanding of how molecules conduct charges is essential for improving circuits, in which individual molecules define the performance of the electronic device.

Despite the enormous progress that has been made in the field of molecular electronics, our understanding of the most fundamental process, charge transport across a molecule, is still surprisingly poor. One of the main problems in taking a close-up look at moving charges on conducting molecules is that the transport process happens on timescales that are out of reach for direct electrical measurements. Electrical probing reveals a lot of information on conduction efficiency and other time-integrated circuit properties, but it does not provide a microscopic picture of what actually happens to a single molecule when it conducts charges. Injection of an electron into a molecule and the subsequent transport of that electron take place on ultrafast timescales. In order to focus in on this process, a method is required that is sensitive to such timescales.

In this program we combine the field of molecular electronics and ultrafast microscopy to study electron transport in single molecules at the ultrafast timescales. This program aims to overcome the experimental challenges that have held back ultrafast, time- resolved optical experiments on single molecules. We employ a special nanowire circuit optimized for precise optical excitation of so-called surface polaritons. Fine control of surface plasmon polariton excitation enables the injection of electrons into nanojunctions spanned by molecular bridges. Our program is built on a systematic optimization and characterization of laser-assisted electron injection through surface polarition control, and includes light- synchronized, time-resolved experiments designed to uncover the hitherto hidden molecular dynamics associated with the electron transport process. Findings that result from this research program are of direct relevance to advancing the understanding of charge transport through molecules, and provide essential insights for tailoring molecular properties for the design of tomorrow's molecular circuits."

Optical Spectroscopy at the Spatial Limit

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Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$175,000

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 coupling light to 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 single molecule fluorescence, the primary steps of electron transfer to a single molecule, and photo-induced changes in single molecules.

Four focused activities are in progress during FY 2011, and all are designed to probe and image the dynamic properties in the interior of single molecules and artificially created nanostructures. The activities are (1) spatially, spectroscopically, and temporally resolved photon imaging; (2) direct measurement of photo-induced tunneling current; (3) photo-induced electron tunneling in the time domain; and (4) two-electron induced light emission. We are investigating the time dependence of photo-induced changes in a single oxygen molecule adsorbed on a silver surface and light emission from titanium dioxide and molecules adsorbed on this surface. These experiments are expected to provide a fundamental understanding of matter by revealing them in previously unattainable regimes of space and time. Furthermore, knowledge of the coupling of light to nanoscale objects bring us one step closer toward the realization of efficient conversion of sun light to energy, a broad range of optoelectronics and plasmonics, and economically competitive photocatalysis.

Spin-Forbidden Chemical Reactions in Catalysis from First-Principles

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Students:	0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$56,000

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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We are using first-principle computational methods based on density functional theory (DFT) to investigate the catalytic formation of H_2O_2 from gas phase H_2 and O_2 over Pd_n clusters. H_2O_2 is an important industrial oxidant that is currently produced via environmentally unfriendly reactions. One practical aim of this project is to aid in the development of “green” approaches to producing H_2O_2. A more fundamental aim is to better understand nanoparticle-based heterogeneous catalysis in general, via systematic modeling of reactions using accurate theoretical methods. We are interested in establishing the important descriptors of reactivity on metal nanoparticles.

The work is proceeding in phases. In the initial phase, we tested a variety of DFT methods to determine which provides the best description of Pd_n cluster chemistry. The calculations were carried out using the NWChem code. An array of calculations indicated that the PBE0 functional gives the best agreement between computed and measured properties for small Pd_n clusters.

We next explored the preferred binding sites of O_2 and H_2 molecules on Pd_n and how these depend on the size and spin state of the clusters. O_2 binds molecularly on cluster edge sites with a binding energy of about 1.2 eV. The barrier to O_2 dissociation is large, at 2.1 eV. These results vary little between cluster sizes n = 2 to n = 55. By contrast, H_2 dissociates without a barrier on bare clusters. The dissociated atoms cover edges and/or triangular faces on the cluster surfaces. The binding energy for dissociative adsorption of H_2 varies significantly with cluster size, from 1.7 eV for the smallest sizes, to about 0.8 eV for Pd_{13}. We are currently investigating the effect of saturation on the adsorption of H_2 and O_2. This involves a systematic determination of the maximum number of adsorbates that can bind as a function of cluster size. Interestingly, there is a switchover from dissociative to molecular adsorption for hydrogen dimers as additional H_2 are added. On Pd_7, for example, the first two dimers dissociate, and remaining H_2’s bind molecularly.

The current phase of the project involves exploring the reaction mechanisms for H_2O_2 production on Pd_n. A key step is H migration over the cluster to form Pd_n-H-O_2 intermediates. We find that adsorbate coverage has a significant effect on migration barriers for the smallest clusters. We are also investigating the importance of spin on reaction steps and are exploring methods for predicting rates for steps that involve transitions between spins.

Chemical Imaging and Dynamical Studies of Reactivity and Emergent Behavior in Complex Interfacial Systems

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This new 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 (AFM) imaging, scanning tunneling local electronic spectroscopy (STS), 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 proposal 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.

Interfacial Oxidation of Complex Organic Molecules

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We are fabricating a new experiment to study the oxidation of surfactants coating water droplets. This instrument is designed to produce a stream of saline-water droplets that are coated with organics, to size-select them, and to inject them into an atmospheric flow tube where they will be dosed with OH radicals. The organic radicals will combine with O_2 and produce a population of peroxyl radicals at the droplet/atmospheric interface. The resulting oxidized particles will be analyzed with a mass spectrometer. A 1 µm saline-water, organic aerosol contains roughly 1010 waters in the core and carries about 107 surfactant $CH_3(CH_2)10CO_2$— ions at the droplet/atmosphere interface. The heat of vaporization of water is 40.7 kJ mol-1 so it takes roughly 1 nJ to vaporize a 1 µm aqueous droplet. The LaserVision OPO is pumped by a YAG laser and delivers 30 mJ/7nsec of 2.94 µm (3400 cm-1) radiation focused to a 1 mm spot. The imaginary part of the refractive index of water provides the absorption coefficient and a 1 µm droplet will absorb 18 nJ of the 10 mJ pulse. There are no organic vibrational modes resonant with the 3400 cm-1 radiation. The absorption coefficient of water, a(H_2O, 2.93 µm), is measured to be 0.88 µm-1 so the optical penetration depth is roughly 1.1 µm. Consequently all of the 18 nJ will be absorbed by the saline-water core of the particle. The surfactant-coated droplet will completely dissociate and release the surfactant negative ions for analysis by a quadrupole mass filter.

Laser Dynamics Studies of Photoreactions on Single-Crystal and Nanostructured Surfaces

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The motivation for the current research program is to examine the photon-initiated reaction mechanisms, half-collision dynamics, and other nonequilibrium-excited dynamics effects, occurring with adsorbates on well-characterized metal-oxide nanosurfaces. The specific goal of our research is to understand photoreactions dynamics on nanostructured and nanocrystal surfaces. Our program, thus far, has developed new synthesis methods for uncapped nanocrystals with specific reconstructions and orientation in a UHV STM instrument. We will now use the tip on our STM or an in situ flood UV lamp to excite either specific sites of these nanocrystals or the overall surface of a nanocrystal, respectively. The resulting chemistry and surface dynamics will be investigated via imaging of the reaction fragments in the vicinity of the reaction events. Additional research tools are time-of-flight detection, XPS, standard UHV probes, in situ TPD, and molecular computational tools. Interaction with the Surface Dynamics Group and Catalysis Group at Brookhaven National Laboratory is on-going. The work is complementary to other programs in TiO_2 nanoparticle synthesis, reactions, and photoreactions at the Fritz-Haber Institute, PNNL, and Harvard.

From the perspective of DOE energy needs, photoexcitation has been of continuing interest for its importance in photocatalytic destruction of environmental pollutants, in several methods of solar-energy conversion, and in a variety of applications of nanotechnology. Our recent work in this program has yielded several new research findings regarding the preparation of nanocrystals, the adsorption of aromatics on TiO_2 surfaces, and the feasibility of tip-induced cleaving of bonds within these molecules.

Photochemistry at Interfaces

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The objectives of the research are to investigate the properties of liquid interfaces motivated by their fundamental scientific and technological significance. Their importance derives not only from their being the special region across which all material and energy must cross in passing between bulk media; due to its molecularly thin dimensions and inherent asymmetry, they have unique chemical, physical, and biological properties that differ from the bulk media that bound it. These include the time independent properties (e.g., chemical equilibria, free energy driving force for adsorption to interfaces, dielectric properties, and electronic and vibrational energy states of interfacial molecules) and time dependent properties (e.g., ultrafast chemical dynamics, energy transfer, molecular motions, and the competing physical and chemical pathways by which molecules in excited electronic states dissipate their energy). To achieve these objectives, we use the interface selective spectroscopies of second harmonic generation (SHG) and sum frequency generation (SFG). We are currently carrying out experiments to measure the free energy and population of molecules that spontaneously adsorb to gold nanoparticles suspended in water, which to the best of our knowledge, has not and cannot be done using current methods. We use femtosecond lasers that enhance the strength of the SHG and SFG signals and provide femtosecond time resolution. With this laser system, we are pumping molecules to excited electronic states and observing intermolecular electron transfer between interfacial molecules in real time. Similarly, we are studying the ultrafast dynamics of interfacial solvation. These experiments are the first ones that measure interfacial dynamics using time resolved vibrational SFG, which provides the analytical sensitivity of a vibrational spectroscopy to probe excited state dynamics at interfaces.

Super Instruction Architecture for Scalable Parallel Computations

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Funding:	$170,000

This project seeks to further develop the Super Instruction Architecture (SIA), an innovative development environment to create parallel software that yields high quality code with exceptional parallel scaling characteristics, and allows parallel programmers to be very productive compared to other approaches.

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, including quantum dots to enable the development of more efficient solar cells, and computation of core-excitation spectra to provide theoretical support for high intensity light sources.

Our accomplishments include several improvements to the basic infrastructure of the SIA and ACES III including an improvement in memory usage by sharing read-only data by processes resident on the same compute node, several enhancements allowing ACES to handle larger molecular systems, and preliminary work to refactor the SIA to exhibit a more modular design with clearer internal interfaces. We have also introduced a Python interface that will allow Python scripting of job flow for users and more convenient access to internals by developers. An eventual goal is to support interfacing ACES III modules with other computational chemistry packages. To help programmers most efficiently use expensive and scarce computational resources, we have developed a tool that generates a performance model of arbitrary SIAL programs from the SIAL source code augmented with measurement data obtained from a small scale execution of the program (on 2 processors). This is challenging because data motion in SIAL programs is highly irregular compared with most applications that have subjected to a serious modeling effort.

The scientific code provided by ACES has been enhanced with optimization of the SIAL code for UHF/RHF CCSD(T), RHF/UHF MBPR(2), RHF/UHF CIS, RHF/UHF EOM-CCSD and EOM-CCSD(T). Highly optimized LCCD(RHF) gradient code has been added. Our experience has demonstrated that we are able to effectively make use of subsegments, a novel feature of SIAL that allow use higher (>4) dimensional arrays and provide ways to improve scaling.

Several advances in the coupled-cluster methods in electronic structure theory and applications have been published. We will briefly describe one example, electronic excited states of nano diamond. The recent work of Delaney, Greer, and Larsson [Paul Delaney, James C. Greer and J. Andreas Larsson, Spin-Polarization Mechanisms of the Nitrogen-Vacancy Center in Diamond, Nano Lett., 10 (2), pp 610–614 (2010), DOI: 10.1021/nl903646p.] on the spin-polarization mechanisms in the nitrogen-vacancy in nano diamond crystals leads to the need for accurate determination of the excited states. Several methods have been tried, but they do not agree on the ordering of the excited state energies. The ordering is critical for application of the nano structure as a storage device. We are now working with these authors to calculate the excited state energies with a more accurate theory than tried so far, namely EOM-CCSD. These calculations have been performed on the Cray XT5 at the Oak Ridge Leadership Computing Facility. Because the calculation involves 300 electrons, some work was needed to make ACES III scale to the necessary number of cores to complete the calculation within the 24 hour queue limit. The model of the nano diamond crystal with nitrogen-vacancy that we use in this calculation is $C_{42}H_{42}N$. One of the research objectives is to increase the size of the nano structure in order to see the trend of the spectrum as the system approaches bulk diamond.

Several versions of ACES III have been released during the reporting period: ACES 3.04 on July 20, 2010; ACES 3.05 on October 12, 2010; and ACES 3.06 on April 14, 2011.

Using Plasmonic Nanoparticles for Improving Solar-Energy Conversion in Bacterio-Rhodopsin and other Systems

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Solar energy is an abundant, free, and open source which can provide Earth's surface with an amount of energy sufficient for the consumption by the whole world's population in an entire year in just 1.5 hours. However, electricity produced by photovoltaics or solar energy converted to fuels such as H_2 is unaffordable to use on such a large scale. In order to reduce the cost per watt of solar electricity, a revolution in photovoltaic technology as well as a breakthrough in the understanding of the basic science involved is essential. Our work focuses on the effects of nanoscale plasmonic metal particles on the radiative and nonradiative electronic properties of other materials, which could be used to improve the efficiency of materials used in solar-energy conversion. Nanoscale plasmonic metal particles (such as silver and gold) are known to support coherent oscillatory modes of their conduction band electrons and produce strong surface plasmonic electro-magnetic fields known as localized surface plasmons. Resonant electromagnetic fields can couple with these modes resulting in photon absorption and/or scattering and the generation of intense electromagnetic near-fields which can enhance a range of optical and electronic processes such as fluorescence, Raman scattering, Förster Resonance Energy Transfer (FRET), and resonant energy transfer between metallic and semiconducting nanoparticles. These phenomena require that the exciton energy of the coupled electronic system overlap with that of the plasmon resonance, which can be excited by visible or near-infrared light in the case of Ag and Au nanoparticles, and that the transition dipole moment of the exciton lie collinear with the dipole moment of the oscillation of the plasmon resonance.

Transition Metal-Molecular Interactions Studied with Cluster Ion Infrared Spectroscopy

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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 Mx+(L)y, where M= transition metals (Fe, Co, Ni, Ag, Au, etc.) in single (n=1) or multiply charged (n>1) states, and L= small molecules such as CO, CO_2, H_2O, C_2H_2, N_2, benzene, etc., are produced in the gas phase environment of a molecular beam by pulsed laser vaporization. Complexes containing a specific number of metal atoms and ligands are size-selected with a specially designed time-of-flight mass spectrometer and their vibrational spectra are measured with infrared laser photodissociation spectroscopy. The resulting spectra determine the shifts that occur upon ligand/adsorbate binding to metal, and how this varies with the number of ligands, as well as the geometric and electronic structures of complexes, the number of ligands in the full coordination sphere around atomic or clustered metal species, and the possible occurrence of insertion or ligand dissociation reactions mediated by the metal center. The experimental data is interpreted through careful comparisons to theory (usually density functional theory) to provide new insights into metal-molecular chemistry.

Room Temperature Single-Molecule Detection and Imaging by Stimulated Emission Microscopy

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Optical studies of single molecules in ambient environments, which have led to broad applications, are primarily based on fluorescence detection. Direct detection of optical absorption with single-molecule sensitivity at room temperature is difficult because absorption is not a background-free measurement and is often complicated by sample scattering. Here we are working on ground state depletion microscopy for ultrasensitive detection of absorption contrast. We image 20 nm gold nanoparticles as an initial demonstration of this microscopy. We then demonstrate the detection of the absorption signal by a single chromophore molecule at room temperature. This is accomplished by using two tightly-focused collinear continuous-wave laser beams at different wavelengths both within a molecular absorption band, one of which is intensity modulated at a high frequency (>MHz). The transmission of the other beam is found to be modulated at the same frequency due to ground state depletion. The signal of single chromophore molecules scanned across the common laser foci can be detected with shot-noise limited sensitivity. This measurement represents the ultimate detection sensitivity of nonlinear optical spectroscopy at room temperature.

Multiscale Investigation of Hydrocarbon Interactions in Porous Spaces

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The amount of energy humans use every year is about equivalent to the energy delivered to the Earth by the Sun in just one hour. This is equivalent to 1.2x10^5 terawatts, and it easily exceeds the rate that man-made machines can produce and use, which is about 13TW. Think about the possibility of having tools that can effectively use a fraction of such energy resources. However, currently only 0.015% of the world's electricity is converted from the Sun. The difficulty in harvesting solar energy lies in the fact that, unlike fossil fuels, sunlight spreads out over a large area and it is hard to collect its energy in high concentration using current technology. Therefore, there is a need for efficient ways to convert solar energy to resolve a foreseeable energy crisis due to a shortage of fossil fuels.

One of the ways is to learn the mechanisms of photosynthesis from plants and bacteria and design bio-inspired materials that can convert solar energy to chemical fuels in a much more efficient fashion. In recent decades a research group led by Gust and others has started to synthesize abundant artificial photosynthetic materials in nanometer sizes. Some of these light-harvesting compounds have promising potentials as chemical fuels. This nano-sized "solar cell" can potentially catalyze water into hydrogen or carbon dioxide into methane by changing into an excited state when it absorbs sunlight. Both hydrogen and methane are desirable fuels for clean energy; however, they only exist for a tiny fraction of seconds in the laboratory. Unless the properties of these light-harvesting nano-sized materials can be managed and contained under ambient conditions for a much longer time, they are far from for a practical use.

Motivated by the need for a better way to manipulate such amazing molecules that have the potential to solve tomorrow's energy problems, we conduct research on the behavior of light-harvesting compounds at an atomistic detail using combined approaches of statistical physics, quantum chemistry, and computers simulations. Particularly, we study a compound that consists of a fullerene (C60) that acts as an electron acceptor, a chromophore that absorbs visible lights, and a carotenoid that acts as an electron donor. However, the challenge comes from the large structural flexibility of a molecular triad that is vulnerable to the interactions with its surrounding solvents. Particularly when the temperature rises, agitated solvent molecules bar the light-harvesting function of a molecular triad. Interestingly, experiments have also shown that the life-time of a molecular triad can be extended when the surrounding solvent composition was altered. The pending issue is obviously related with the dynamical and structural relationship of a molecular triad and its surrounding solvents. However, little is known about such a relationship.

In this research funded by DOE, we propose to characterize the dynamics and structures of a molecular triad at the liquid and solid interface, by theory, modeling, and computer simulations. We will determine the temperature dependence of the structures of the ground state and the excited states of a molecular triad in a solvent box or in a nanosized capsule. We will identify the solvent configurations at the inner solvent shell of a molecular triad as the geometry of the nano-container alters. When such knowledge is available, it can be potentially useful to a better design of light-harvesting materials.

Manipulating Light With Transition Metal Clusters and Dyes

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In this project, we develop and apply state-of-the-art first principles methods to predict electronic and optical properties of two systems of significant scientific and technological interest: transition metal clusters and organic dyes. These systems offer great opportunities to manipulate light for a wide ranging list of energy-related scientific problems and applications. In particular, the investigations are focused in the following areas:

(1) Development and implementation of many-body Green's function methods based on solving the GW-Bethe-Salpeter (GWBSE) equation to examine the excited state properties of transition metal and noble metal clusters. Different approximations made in practical applications of time-dependent density functional theory (TDDFT) and GWBSE result in significantly different predictions for the optical excitations in these systems, especially for transitions involving d electrons. Our research focuses on investigations that are expected to lead to more reliable, numerically stable, and computationally efficient implementations of the GWBSE method, which can capture the essential correlations inherent in d electron systems. The emphasis in the proposed activity is not so much on algorithmic development, but rather our activities center on identifying the optimal set of approximations in the implementations of GWBSE method that will find a balance between accuracy and computational efficiency.

(2) The application of TDDFT and GWBSE to predict electronic and optical properties of a set of organic dye molecules, in free-standing and supported configurations, relevant for dye-sensitized solar cell applications. In particular, in this subproject we focus on the optical properties of brominated perylene diimide dyes, such as Br-PDI and their glycine (BrGly) and aspartine (BrAsp) derivatives. These dyes absorb and emit light in the visible range with high quantum yields, and have good heat and chemical stability. Accordingly, they are promising alternatives to the expensive (Ru-based) metal-driven dye sensitizers for solar cell applications. In collaboration with colleagues in Turkey, we model optical properties of these dyes and investigate the effects of a TiO_2 substrate, in bulk and nanostructed forms, on their absorption properties.

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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The multivariate and complex nature of heterogeneous catalytic systems can confound efforts to characterize the critical electronic and structural features involved in catalysis, which is a fundamentally molecular scale phenomenon. Our research program combines experimental and computational methods to study well-defined cluster models of heterogeneous catalytic materials, with the goal of informing efforts to optimize existing catalytic systems, and to develop new materials for catalysis. The focus of our studies has been transition metal oxide and sulfide clusters in non-traditional oxidation states (surface defect models) and their chemical and physical interactions with water. The application that is currently being modeled is H_2 production from photocatalytic decomposition of water using Group 6 (Mo and W) oxides, and heteronuclear metal sulfides. The experiments and calculations are designed to probe fundamental, cluster-substrate molecular-scale interactions that are governed by charge state, peculiar oxidation states, and unique physical structures.

The general strategy of our studies is as follows: (1) Determine how the molecular and electronic structures of transition metal suboxide and subsulfide clusters evolve as a function of oxidation state by reconciling anion photoelectron spectra of the bare clusters with high-level DFT calculations. Anions are of particular interest because of the propensity of metal oxide and sulfides to accumulate electrons in applied systems. (2) Measure and kinetically analyze cluster reactivity with water. (3) Dissect possible reaction mechanisms computationally, to determine whether catalytically relevant interactions are involved. (4) Verify these challenging computational studies by spectroscopic investigation of observed reactive intermediates. (5) Probe the effect of local electronic excitation on bare clusters and cluster complexes, to evaluate photocatalytic processes.

The overarching goal of this project is to identify particular defect structures that balance structural stability with electronic activity, both of which are necessary for a site to be simultaneously robust and catalytically active, and to find trends and patterns in activity that can lead to improvement of existing applied catalytic systems, or the discovery of new systems.

Understanding Nanoscale Confinement Effects in Solvent-Driven Chemical Reactions

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Our research in the past year has focused on using theory and computation to address how solution-phase chemistry is affected by nanoscale confinement, e.g., in porous silica glasses. These systems feature both the appearance of new fundamental phenomena and a wide range of potential applications, including catalysis, sensing, separations, electrochemistry, and optical materials. We have examined several processes in nanoconfined liquids: (1) solvation dynamics, (2) proton transfer, and (3) reorientational dynamics. The latter has led us to also investigate phenomena in liquid alcohols.

Dynamical properties of confined (and bulk) solvents are often probed by time-dependent fluorescence (TDF) measurements that report on the timescales for solvent rearrangement around a dye after a charge-transfer transition. In nanoconfined solvents, results are generally marked by dramatic changes relative to the bulk solvent; long time scales not seen in the bulk, often as long as hundreds of picoseconds or several nanoseconds, are observed in the TDF signal. We have used atomistic models of amorphous silica pores and both model and atomistic dyes to simulate TDF results and the underlying free energy surfaces. One focus has been the position distribution of the dye, its dependence on the electronic state, and the relevance for TDF. Simulations on a variety of systems indicate that a state-dependent solute distribution is general, due to a combination of the surface interactions and position-dependent solvent polarity. On the other hand, while this observation is broadly relevant to chemistry in confined solvents, it may not always be manifested in TDF measurements.

We have also studied proton transfer (PT) reactions in nanoconfined solvents using an umbrella sampling approach based on the proton vibrational energy gap. The results on a model phenol-amine PT reaction complex in a solvent within a nanocavity are consistent with those obtained from calculations based on a collective solvent coordinate. However, the vibrational energy gap differs in the ensemble of transition state configurations it generates and also provides insight into the vibrationally nonadiabatic coupling for the PT reaction. This vibrational gap may be a general way to sample PT transition states in complex systems where the solvent coordinate is not the full reaction coordinate.

We have investigated the reorientation dynamics of water confined within nanoscale, hydrophilic silica pores in collaboration with Dr. Damien Laage (Ecole Normale Superieure, Paris, Fr). The effect of surface hydrogen-bonding and electrostatic interactions were examined by comparing with both a hydrophobic pore and bulk water. We found that the OH reorientation in water is slowed significantly in hydrophilic confinement compared to bulk water, and is well-described by a power-law decay extending beyond one nanosecond. In contrast, the dynamics of water in a hydrophobic pore are more modestly affected. A two-state model, commonly used to interpret confined liquid properties, provides a good fit of the orientational decay. However, our analysis shows that the molecular-level assumptions are not supported: the interface dynamics is markedly heterogeneous, especially in the hydrophilic pore and there is no single interfacial state with a common dynamics.

Similar simulations of the reorientational dynamics of confined alcohols led us, also in collaboration with Dr. Laage, to consider the mechanism of OH bond reorientation in the corresponding bulk liquids, specifically methanol and ethanol. We found that the extended jump model, recently developed for water, describes the OH reorientation in these liquids. The slower reorientational dynamics in these alcohols compared to water can be explained by two key factors. The alkyl groups on the alcohol molecules exclude potential partners for hydrogen bonding exchanges, an effect that grows with the size of the alkyl chain. This increases the importance of the reorientation of intact hydrogen bonds, which also slows with increasing size of the alcohol and becomes the dominant reorientation pathway.

Structural Dynamics in Complex Liquids Studied with Multidimensional Vibrational Spectroscopy

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Funding:	$559,000

Water is a unique liquid due to the fact that it can form up to four hydrogen bonds, creating a structured tetrahedral network of molecules that evolves on ultrafast time-scales as hydrogen bonds interconvert. It is the fluctuations of this network that allow water to rapidly solvate nascent charge and to participate in chemical reactions. Moreover, it is predicted that the breakage and rearrangement of hydrogen bonds plays a major role in charge transport in water and is an intrinsic element of proton and hydroxide transport. 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 aqueous charge transport and reactivity. Our work during the past year can be divided into three topics: (1) reorientational dynamics of water molecules during hydrogen bond exchange, (2) temperature-dependent hydrogen bond dynamics in water, and (3) construction of a 2D IR pump-probe interferometer using broadband IR to study the dynamics of proton transport in aqueous acids and bases.

Our previous work has suggested that hydrogen bonds in water rearrange in concerted switching events that include large angle excursions in hydrogen bond alignment and a transition state that has bifurcated hydrogen bond character. To test the predictions of the orientational dynamics during switching we performed polarization sensitive nonlinear experiments. We measured 2D IR spectra of HOD in D_2O in different polarization geometries to determine the two-dimensional anisotropy. The 2D IR anisotropy correlates the initial and final OH stretch frequency with a corresponding orientational anisotropy, allowing us to understand the extent of rotation water molecules undergo while changing HB environments. from our measurement, we estimate the average reorientation for hydrogen bond switching to be ~ 20 degrees and maximum rotation to be ~ 46 degrees, within 100 fs. This observation is consistent with earlier work from our group that showed that HB switching is a concerted process where strained HB geometries are transiently visited species during HB exchange.

We have also performed studies to reveal how water participates in the dynamics of hydroxide ion transport. This ion undergoes anomalously fast diffusion due to the ability to accept a proton from neighboring water molecules leading to the translocation of the ion via the Grotthuss mechanism. Simulations have suggested that hydrogen bond rearrangements play a key role in guiding proton transfer processes involving these ions. Our measurements of 2D IR spectra of dilute HOD in concentrated $NaOD:D_2O$, displayed a rapid loss of intensity on the low frequency side of the 2D lineshape with a timescale of 100 fs. With the aid of empirical valence bond (EVB) molecular dynamics simulations from Todd Martinez's group at Stanford University, we identified this feature to be from nearly equally shared proton species that exhibit highly red-shifted v=0-2 transitions that enter the bandwidth of our infrared pulse. By a 100 fs, this shared proton species relaxes to a configuration where the proton is localized on a water molecule, leading to a blue-shifting of the v=0-2 transition out of the bandwidth of our pulses. Thus, the spectral feature exhibiting a 100 fs relaxation was attributed to the shared proton species in aqueous hydroxides. 2D IR surfaces at longer waiting times of >1 ps were also measured to reveal the chemical exchange processes between OH- and HOD. Using exchange kinetic models to self-consistently fit our magic angle pump-probe, peak shift, linear IR and 2D IR spectra for dilute HOD in a range of concentrations of NaOD/D_2O, we quantified this chemical exchange process to occur on a timescale of at least 3 ps.

Theory of the Reaction Dynamics of Small Molecules on Metal Surfaces

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Funding:	$133,000

Our overall objective is to develop realistic theoretical models for molecule-metal interactions important in catalysis and other surface processes. The majority of our recent efforts have focused on the dissociative chemisorption of methane on Ni surfaces, which is the rate-limiting step in the chief industrial process for production of molecular hydrogen. Our initial studies of methane dissociation on Ni(111) used DFT to compute the barrier height 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 increases and decreases, respectively. High dimensional 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 can accurately add these effects of thermal lattice motion to static-lattice calculations.

Over the past two years we have made significant progress on this problem, using a formulation based on the Reaction Path Hamiltonian. In this approach, one locates the reaction (minimum energy) path for reaction, and implements a normal mode analysis at several points along this path. This leads to a full-dimensional potential that includes all 15 molecular degrees of freedom, and that accurately describes the normal vibrational modes. We recast this Hamiltonian into a close-coupled wave packet form by expanding the wavefunction in the adiabatic vibrational states of the molecule. Time-dependent quantum dynamics on this 15-DOF Hamiltonian, for methane dissociation on Ni(100), showed that the symmetric stretch significantly softens at the transition state, and is strongly coupled to the reaction coordinate. As a result there is a large vibrational efficacy for this mode, which has been observed by two experimental groups. We have demonstrated how these large efficacies for vibrational enhancement are related to transitions from higher to lower energy vibrationally adiabatic states, or to the ground state, with the excess energy going into motion along the reaction path, increasing the tunneling (reaction) probability. We have just completed similar studies on Ni(100), and our model is capable of reproducing and elucidating not only the reactivity of ground state and vibrationally excited molecules, but also the variation with temperature as recently measured by the Utz group at Tufts.

We have also been studying the reactions of H atoms with graphite and graphene, important in the formation of molecular Hydrogen on graphitic dust grains in interstellar space, the etching of graphite walls in fusion reactors, and the modification of the electronic properties of graphene. Different models for computing H sticking (physisorption) probabilities were developed and tested, and a recently accepted paper showed that there is an anomalously large sticking probability on graphene at low energies and temperatures.

Modeling Molecular Electron Transport for Thermal and Photo Energy Conversion

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The goal of the research program is to provide reliable electron transport (ET) modeling and thereby to advance transport control abilities. The resulting insight is used to design schemes in the area of photovoltaics (PV) and thermoelectric (TE) energy conversions. We aim to provide fundamental understanding of the ET process, to explain experimental measurements and to provide predictions for designing new experiments.

We model TE properties of molecular scale junctions. One important parameter determining the TE conversion efficiency is the thermopower. The thermopower is a material property that relates the generated voltage upon temperature biasing conditions applied across the device. It also elucidates the type of conductance supported by the device when voltage biasing is applied. We have provided modeling of the thermopower on molecular junctions that were measured experimentally by our collaborators (Reddy). The combined experimental and computational approach demonstrates convincingly that the conductance mechanism depends on the molecular contacting group to the electrodes. [Tan et al, JACS 2011]

In following TE related studies we analyze the relationships between the basic polarization effects as determined by the electrode-contacting molecular species and the thermopower. These relationships strongly affect the conductance mechanism. In another pending publication we introduce a novel device concept that combines spin filtering with thermal transport in molecular scale junctions.

We also achieve progress on fundamental aspects in modeling electronic transport. We consider ways to enhance the convergence of non-equilibrium Green's function (NEGF) that is combined with density functional theory (DFT). The DFT-NEGF approach is considered the cutting edge in modeling electron transport. We highlight aspects that are required to be addressed for achieving reliable modeling. Our studies relate symmetry in the models as a source for an artifact that must be avoided in proper modeling. We also develop with our collaborators a DFT-NEGF approach to handle solvation effects on the transport.

In another thrust, we model photo induced electron transfer in materials that are promoted as candidates for photovoltaic applications. In these projects we use range separated functionals to describe charge transfer processes within time-dependent DFT. We use our approach to resolve the charge transfer process in the tri-metal centers systems pursued by Prof Khalil (University of Washington). In another recent project we treat charge transfer states that are hidden by inherent system symmetry. We then demonstrate the success of the novel functionals in treating these hidden states by following different modes to break the symmetry. The study provides important insight to develop functionals that treat properly charge transfer.

Computational Modeling and Theory Development of Energy and Charge Flow Dynamics in Photosynthetic Units and Conjugated Polymer Systems

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Funding: $82,000

The research consists of two related projects. One is to elucidate the design principles of highly efficient energy flow dynamics in the photosynthetic unit (PSU) of purple bacteria. The other is to develop theories of excitation and charge flow dynamics in major conjugated polymer (CP) systems used for plastic solar cells. These efforts are respectively motivated by two long-term goals: (1) help develop biologically inspired, novel solar energy conversion devices and (2) provide theoretical insights for how to enhance the efficiency of plastic solar cell devices.

The research on the energy flow dynamics in the PSU involves understanding the exciton relaxation dynamics within each light harvesting complex and modeling the energy flow dynamics between different light harvesting complexes. For the former, theoretical development and refinement of exciton-bath Hamiltonians of light harvesting complexes is in progress through modeling and analysis of spectral lineshapes. The developed models can be used directly for the calculation of energy transfer rates based on a well-established theory of multichromophoric Forster resonance energy transfer (MC-FRET). Additional theoretical effort has been made to develop multichromohproic coherent resonance energy (MC-CRET). Comparative application of MC-FRET and MC-CRET to the energy flow dynamics in the PSU will help understand the role of quantum coherence in the efficiency and robustness of the biological light harvesting process.

The research on CP primarily involves developing a theory of lineshape for strongly coupled exciton-bath model and a theory of charge flow along a torsionally flexible wire. In addition, collaborations with spectroscopy groups are being developed for better understanding of exciton and charge flow dynamics in single CP systems.

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

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 inter-facial charge distribution is the result of the chemical bonding between solute and metal atoms, and therefore cannot be accurately calculated with the use of semi-empirical classical force fields. We will study in detail the structure and dynamics of aqueous electrolytes at metallic interfaces taking into account the effect of the electrode potential. The electrode potential will be set by using the methodology already developed for the study of electronic transport in nano-structures. The ab-initio molecular dynamics (AIMD) simulations will be performed with the Siesta program. An interface for the combination of both methods in AIMD simulations will be developed. Methods based on Density Functional Theory will be adapted and tuned for efficient and accurate AIMD calculation of metal-electrolyte interfaces. The PI has a well established record of applying DFT to this problem and has already successfully developed a formalism within the Siesta program to accelerate molecular dynamics simulations of metal-water interfaces. The PI also has a broad experience in the field of electronic transport in nanostructures, with 4 high profile articles published in this area. The combination of these two backgrounds makes the Pl a perfect candidate to successfully execute this project.

Optimizing Interfacial Charge Transfer in Photocatalytic Water Splitting Devices

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Funding:	$49,000

Solar water splitting, driven by novel semiconductor/metal nanostructured devices, has the potential to provide a clean, carbon-free energy cycle wherein sunlight converts water into hydrogen fuel, with oxygen the only byproduct. The challenge of optimizing the performance of such devices must be met on multiple fronts. While most efforts have focused on improving the catalytic activity of the water-immersed surfaces and tuning the semiconductor band gap for maximal absorption of sunlight, it is also essential to understand the chemistry of the surfaces in fully solvated environments. The research in this proposal combines first-principles simulations of water on surfaces with quantum chemistry methods to analyze the electronic structure of solvated surfaces. The focus of the research is to understand the links between water dissociation and photocatalytic activity.

Single Molecule Chemical Imaging at Femtosecond Time Scales

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Funding:	$600,000

Imaging molecular functionality with atomic spatial resolution and femtosecond 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. Furthermore, scanning tunneling spectroscopy (STS) only provides indirect chemical identification via measurements of the electronic density of states. 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. This SISGR program seeks to overcome the respective limitations of UHV STM and laser spectroscopy by integrating these techniques into one experimental platform. This interdisciplinary challenge is being pursued by a multidisciplinary and multi-institutional team with expertise in UHV STM, STS, SERS, femtosecond pump-probe laser spectroscopy, and innovative theoretical and computational modeling techniques. Ongoing work is addressing fundamental light-matter interactions at the single molecule limit including nonequilibrium electron transfer, energy transfer, reversible photochemistry (e.g., photoisomerization), and irreversible photochemistry (e.g., light-driven desorption, dissocation, and polymerization). Since the systems and substrates to be studied are directly applicable to dye-sensitized solar cells, organic photovoltaics, and photocatalysis, this research program will inform efforts to improve alternative energy technologies in addition to impacting the fundamental scientific goals outlined in the DOE Grand Challenges.

Surface Plasmon Enhanced Chemistry

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Funding:	$180,000

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. This work builds on past work by this team that has developed computational electrodynamics methods 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. The new research associated with this grant is 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.

Projects completed through October 2011 have been divided into three groups: (1) understanding nonlocal dielectric effects in plasmonic systems, (2) developing a theory of plasmon-enhanced photo-induced electron transfer (PIET) processes, and (3) modeling electromagnetic hot spots for plasmonic nanostructures for the interpretation of optical and electron loss experiments. Our studies of nonlocal dielectric effects are based on a new computational method that was developed just before the beginning of the grant which enables us to perform computational studies of light interacting with nanoparticles of any shape using a variant of the finite-difference time-domain method. Our work for the DOE grant has been concerned with nanoparticle dimers with a small gap. Such structures show intense hot spots that can contribute to important plasmon-enhanced chemical processes. Our calculations show that including nonlocal effects (which is a more sophisticated theory than the standard local approach, thereby mimicking quantum effects in what is otherwise a classical theory) leads to smaller hot-spot enhancements, but preserves much of the resonant structure of the local results.

Our studies of PIET processes are an attempt to develop a new theory that describes photoexcitation followed by electron transfer in plasmonic particles. The new theory we have developed is based on Marcus theory, but with electronic matrix elements that are determined by a time-dependent perturbation theory approach using real-time time-dependent density functional theory with constraints that allow one to define donor and acceptor states. An approach for including the electrodynamic response of a nearby nanoparticle has also been developed.

We have modeled the electrodynamics of a number of nanoparticle structures of interest to surface enhanced photochemistry using conventional local-dielectric methods and theories such as T-matrix theory and the discrete dipole approximation. In one application, we have examined the response of nanoparticle dimers in the near-infrared region of the spectrum to determine how one can achieve larger field enhancements at longer wavelengths. In a second application, we have studied wedge-shaped plasmonic structures that are of interest for tip-enhanced plasmonic effects, showing how enhancement varies with wedge structure and with wavelength. And in a third project, we studied rod-shaped nanoparticles to model electron energy loss measurements and the ability of these measurements to determine the structure of the electromagnetic near-field in the presence of multipole plasmon resonances.

Reaction Field Model for Treatment of Solvation in Electronic Structure Calculations

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Funding:	$138,000

This project involves theoretical development of a comprehensive reaction field model and accompanying computer program to enable accurate and efficient implicit treatment of solvation effects in electronic structure calculations on chemical and spectroscopic properties of a solute, with particular application to water.

Computational Design of Metal Organic Frameworks for Photocatalytic Reduction of CO_2

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Funding: $45,000

REACTION MECHANISMS FOR MOF CATALYTIC ACTIVITY

The area of MOF-based catalysis is still in an immature phase due to the lacking of robust MOF material exhibiting catalytic activity. Theoretical understanding of the reaction mechanism should not only help us to understand the catalytic activity of the material, but also provide useful information to design materials with better performance. Herein, we report our study of the catalytic activity of the ZnMn-RPM MOF. The goal of our study was to identify the reaction mechanisms for styrene epoxidation within ZnMn-RPM. The catalytic activity of this material for this reaction was observed experimentally, but the reaction mechanism was, until our work, unknown. Our findings have been summarized below:

(1) The epoxidation of styrene within ZnMn-RPM MOF was found to proceed through a two-step mechanism. In the first reaction step, the oxidant (2-(Tert-butylsulfonyl)iodosylbenzene) reacts with ZnMn-RPM by transferring an oxygen atom to the Mn site within ZnMn-RPM. During the second reaction step, the oxygen atom is transferred from the Mn site to styrene and forms styrene epoxide.

(2) The transition states for the two reaction steps were identified using the dimer method with the DFT-PBE functional, as implemented within VASP. The energy barriers of the two reactions are about 0.10 and 0.33 eV, respectively, much smaller than the gas phase epoxidation barrier of 1.96 eV that we computed from the same method.

Coordinating Experiment and Theory to Understand How Excess Electrons Are Accommodated by Water Networks Through Model Studies in the Cluster Regime

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Funding: $109,000

Our program exploits size-selected clusters as a medium with which to unravel molecular level pictures of key transient species in aqueous chemistry that mediate radiation damage in chemical and biological systems. Primary among these processes is the nature of the excess electron (hydrated electron) and elementary steps by which the water network mediates electron capture onto secondary scavengers such as O_2 and CO_2. Key to our efforts in this area is a strong coupling between experiment (Johnson, Yale Univ.) and theory/simulation (Jordan, Univ. Pittsburgh). We continue our studies aimed at elucidating how the shape of the water network controls the excess electron binding properties, We are expanding the scope of the program to include the fundamental chemistry needed for the conversion of solar energy to fuel. For example, we are using spectroscopic and studies and computer simulations to characterize the key reaction intermediates in the reduction of CO_2 by water clusters with excess electrons. We are also engaged in studies designed to elucidate processes where electron capture promotes proton transfer. The vibrational spectra of such systems tend to display the consequences of strong coupling between high frequency modes associated with chemical bonds and low-frequency intermolecular vibrations making computational studies essential for unraveling the experimental spectra.

Studies of Surface Adsorbate Electronic Structure and Femtochemistry at the Fundamental Length and Time Scales

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Funding:	$140,000

We have investigated the femtosecond time scale electron and nuclear dynamics in photodesorption of alkali atoms from noble metal surfaces by time-resolved two-photon photoemission (TR-2PP) spectroscopy. In the zero coverage limit, alkali atoms chemisorb on metal surfaces in ionic form. Photoinduced charge transfer excitation with ~3 eV photons prepares alkali atoms in their neutral state at the position of the ionic ground state. The strong Coulomb repulsion between neutral alkali atoms and their image charges initiates dissociative wave packet motion. Photoexcitation of the excited state with a delayed 3 eV probe pulse can induce photoemission from the evolving excited state.

In the case of the Cs/Ag(111) system, pump-probe two-pulse correlation measurements (2PC) indicate unusually long lifetime for the 6s resonance of Cs, which make it possible to follow the photodesorption dynamics for several hundred femtoseconds. Below the time zero energy of 6s resonance, 2PC measurements follow nonexponential kinetics that can be modeled with an exponential rise and decay. If we attribute the rise to the nuclear wave packet motion and the decay to the resonant charge transfer from 6s state to the conduction band continuum of the metal substrate, we would conclude that the nuclear wave packet motion as the excited electronic state decays on ~200 fs time scale and the bond length increases by 0.7 Å. However, the situation is not so simple; 2PC measurements as a function of photoemission angle show that the observed kinetics measurements are strongly emission angle dependent. For low-density alkali atoms, one would expect to measure the same excited state population independent of the emission angle. Therefore, the angular dependence must have a different origin, most likely the electron rather than nuclear dynamics. The angle dependence of 2PC measurements arises either from the evolution of the electronic wave function in the intermediate state, or the electron tunneling effects in near threshold photoemission. We are investigating these possibilities by ultrafast photoemission momentum microscopy, at the MPI for Microstructure Physics and by theory.

CMSN Structure and Dynamics of Water and Aqueous Solution in Materials Science

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Funding:	$105,000

The goal of this computational research team 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 to other U.S. Universities, to National Laboratories and to major international research institutions. This activity was initiated with a kickoff workshop held at the Princeton Center for Theoretical Science (PCTS) on December 6-8, 2010. The second workshop on the series will take place at the Talaris Conference Center in Seattle on February 10-12, 2012. A third workshop will be held at UC Davis in 2013 at the end of the funding period for this grant.

To date the following research highlights can be listed:

(1) The effects of hybrid DFT functionals, of Van der Waals interactions and of quantum nuclei on the structure of liquid water have been investigated. When all of these effects are included the pair distribution functions and the structure factors predicted by theory get very close to those extracted from diffraction experiments. Current and future work along this line should help to better elucidate the implications of these results on major debated issues on the microscopic structure of water.

(2) Hybrid DFT functionals have been found to improve substantially the agreement with experiment of the calculated IR spectra within the harmonic approximation. Future work will help to better understand the role of nuclear quantum corrections on the IR spectra.

(3) The optical and the x-ray absorption spectra of a variety of water systems in condensed phase have been calculated using a COHSEX approach developed at Princeton and a Bethe-Salpeter approach developed at the University of Washington. The systems studied include crystalline ice (with and without proton disorder), liquid water, low-density and high-density amorphous ices. When good structural models (including zero-point motion) and accurate electronic screening models are combined, unprecedented agreement is found between theoretical and experimental spectra. Future work will focus at identifying the microscopic structural information that is behind the observed spectral features.

Interactions, Phase Equilibria and Self-Assembly in Ionic Systems

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Funding: $120,000

The research project supported by this award focuses on studies of interactions, phase transitions and self-assembly in ionic systems, with special emphasis on the precise determination of free energies and the characterization of phase and conformational transitions. In particular, the main objectives of the proposed work will be to (a) obtain effective interaction potentials that represent accurately activity coefficients in concentrated salt solutions, (b) develop and apply a simulation methodology for Donnan equilibria based on a combination of the reactive canonical and Gibbs Monte Carlo techniques, (c) study forces and structure formation near and between charged surfaces with ionizable groups, (d) investigate micellization in ionic surfactants, (e) model sorption and formation of ionic domains in ionomers, and (f) obtain accurate phase diagrams for polyelectrolyte and charged colloidal particle systems, including formation of solid phases. These topics form a logical progression with multiple common themes and synergies in computational methods and models. The project takes advantage of powerful computational techniques developed with prior DOE support, while striving to break new ground both in terms of simulation method development and the selection of physical systems for study.

Optimizing New Materials for Solar Energy Conversion Via Quantum Mechanics

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Funding: $144,000

We have launched a major research effort to use quantum mechanics techniques to search for robust, efficient, and inexpensive new materials for photovoltaics (PVs) 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 optical and photoemission band gaps, character of valence and conduction band edge states that determine nature of the carriers, electron-hole pair lifetimes, electron and hole conductivity, etc. The cost-efficiency tradeoff for PV materials based on ultrapure silicon or tandem semiconductor cells motivates a look at new options beyond traditional main group semiconductors. Limiting oneself to abundant elements constrains our design space and hence we are focusing primarily on first row transition metal oxide parent materials, suitably doped or alloyed with other abundant elements to optimize properties. Fully ab initio schemes for calculating all key properties are being constructed and validated. Design principles that will limit carrier trapping and optimize electron-hole pair lifetime and band gap magnitude, are being developed. The work is revealing which dopants or mixed oxides are most likely to provide solar energy conversion materials that optimize the cost-performance tradeoff.

Towards Linear Scaling Electronic Structure via Partition Density Functional Theory, with Application to Electrochemical Capacitors

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Funding: $103,000

The goal of this project is to develop a computational scheme that is accurate and efficient for the calculation of the electronic-structure properties of systems made of weakly-interacting fragments, scaling linearly with system size. The new scheme will be applied to model systems of disordered carbon with the goal of improving our understanding of the physics of carbon-based electrochemical capacitors when the pores have diameters between 1 and 2 nm.

The project involves (1) demonstrating linear scaling of local approximations and convergence of the algorithm, (2) understanding and quantifying the errors via calculations on model systems, (3) implementing the algorithm into a flexible quantum-chemistry code, (4) using the new methodology to investigate the transferability of fragments in preparation for the main application, and (5) determining the pore-size distributions that maximize the capacitance of nanoporous carbon materials and thus contributing to the search for optimal carbon-based electrochemical capacitors.

This project will contribute to basic-energy research at two levels. First, it will shed light into the physics of nano-porous carbon materials. Second, it will deliver a new tool for the ab-initio calculation of electronic-structure properties of systems made of weakly-interacting fragments. This tool will be invaluable for addressing complex problems in a wide variety of fields, ranging from molecular biology to materials engineering.

Accurate Band Gaps for Tailor-Made Photovoltaic Materials

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Solar energy is a clean, renewable, carbon-neutral source of power that is likely to play an increasingly important role in the nation’s energy infrastructure. While solar radiation is in abundant supply, photovoltaic devices for converting it into electricity are currently quite expensive. Designing cheap, efficient solar cells requires addressing a host of issues. The photovoltaic material, which converts absorbed photons into excited, mobile electrons, must be able to absorb light across the entire range of wavelengths emitted by the Sun. The material must have a high carrier mobility relative to the excited electron’s recombination time, so that electrical energy can be transferred out of the cell before it is lost. The choice of photovoltaic material is thus a critical part of the design of solar cells. Intermediate-band photovoltaics, which can more efficiently capture photons of different wavelengths, are a particularly appealing approach. Experimentally investigating the broad range of candidate materials is a daunting task, however. Calculations modeling candidate materials can be performed at less cost than experiments. The results can be used to help focus the direction of subsequent experiments.

We propose to develop a reliable, computationally tractable, black-box electronic structure method for predicting the optical absorption of novel, tailor-made, intermediate-band photovoltaic materials. Our screened hybrid density functional approximations already offer a reasonable balance between accuracy and affordability for such predictions. We propose to further develop these theoretical tools and test them for existing and proposed photovoltaic materials. With efficient methods for predicting optical absorption spectra, we can computationally prescreen the huge array of candidate photovoltaic materials, enabling experimentalists to focus on the most promising candidates.

Liquid and Chemical Dynamics in Nanoscopic Environments

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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, e.g., 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 biology, water is found in crowded environments, such as cells, where it hydrates membranes and large biomolecules, as well as in pockets in proteins. In geology, interfacial water molecules can control ion adsorption and mineral dissolution. Embedded water molecules can change the structure of zeolites used as catalysts.

Water's unique properties can be traced to its formation of an extended hydrogen bonding network. Water molecules can make up to four hydrogen bonds in an approximately tetrahedral arrangement. However, the hydrogen bonded network is not static. The network evolves constantly on a picosecond time scale by the concerted dissociation and formation of hydrogen bonds. This rapid evolution of water’s hydrogen bond network enables processes ranging from proton diffusion to protein folding. While a great deal is know 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. In addition, important processes such as proton transport, which is necessary in fuel cells, are dramatically changed when they do not occur in bulk pure water.

A variety of nanoconfined water systems and interfaces, such as reverse micelles, lamellar structures, polyelectrolyte fuel cell membranes, and sol-gel glasses as well as room temperature ionic liquids will be investigated using ultrafast two dimensional infrared (2D IR) vibrational echo techniques, and polarization and wavelength selective IR pump-probe experiments. 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. Greatly increased understanding will be obtained by studying a variety of nanoconfined and interfacial systems that have a wide range of properties.

The important process of proton transfer, which is central in technological, chemical, and biological systems will be studied in nanoconfined systems using time resolved ultraviolet and visible spectroscopies. In systems such as polyelectrolyte fuel cell membranes, protons must be transported through nanoscopic channels. Proton transport is intimately related to the hydrogen bond structural dynamics of water. 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 will be substantially enhanced.

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

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Charge transfer excitation plays an important role in photovoltaic and photocatalytic processes. An accurate description of the excited states is necessary for reliable theoretical predictions related to these processes. We have developed a density functional theory based method to accurately describe the charge transfer excited states for large molecular systems. An assessment of the performance of our method on a number of donor-acceptor systems in the gas phase has shown its accuracy, efficiency, and advantage over other methods such as time-dependent density functional theory. For a direct comparison with experimental values obtained from cyclic voltametry, our calculations require the inclusion of solvent molecules that can play a very important role in stabilizing charge transfer excited states. These states generally have large dipoles that can polarize the solvents. The solvent molecules in turn produce a reaction field that stabilizes the excited state. This effect is significant and cannot be ignored if one strives to obtain accurate excitation energies. We are implementing a quantum mechanical-molecular mechanical approach to reliably obtain the stabilizing effect of the solvent on the charge transfer excited state of a donor-acceptor solute system.

A Single-Molecule Approach for Understanding and Utilizing Surface and Subsurface Absorption to Control Chemical Reactivity and Selectivity

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Heterogeneous hydrogenation reactions are among the most scientifically and technologically important chemistries and play a major role in the petrochemical, pharmaceutical, and food industries. While the reactions pathways themselves are often very complex, very basic steps often dictate important parameters like activity and selectivity. Recent research has hinted that the traditional picture of chemical reactions proceeding via only surface-bound species is totally inadequate in describing such systems. Evidence is gathering that subsurface species like hydrogen and carbon are sometimes more reactive and can even have a greater influence on the reaction outcome than surface-bound reactants. Therefore, elucidating the atomic-scale geometry, electronics, and chemistry, both on and under the surface of catalytically important metals and alloys, will prove transformative in advancing current catalytic technology, cutting down on waste products, and helping facilitate more energy-efficient conversion to products.

This project exploits and builds on our recent findings that (1) individual, isolated atoms like Pd in catalytically important alloys can be very active for key steps in hydrogenation chemistry; (2) individual hydrogen atoms, both on and under the surface of Pd metal, can be imaged and manipulated at the atomic-scale; and (3) single enantiomers of a chiral molecule can be distinguished based solely on scanning probe height measurements allowing enantiospecific reactions to be monitored in situ at the single-molecule level. These unique capabilities will allow the roles of surface and subsurface hydrogen in both regular and enantioselective hydrogenation reactions to be interrogated at a new level of detail.

We have demonstrated that single atom alloys can act as very selective hydrogenation model catalysts. The mode of action involves the facile dissociation of H_2 on individual Pd atoms and subsequent spillover of H atoms onto the Cu(111) surface. The selective hydrogenation of alkenes and alkynes takes place on the bare Cu(111) surface where H atoms are weakly bound. Our results demonstrate that individual, isolated noble metal atoms can substantially influence the catalytic properties of less reactive metals, to the extent of converting an entirely inactive surface to an effective catalyst. From a practical application standpoint, the small amounts of precious metal required to produce single atom alloys generate a very attractive alternative to traditional bimetallic catalysts. While we have used a surface science approach to directly visualize the atomic-scale structure of the active sites and relate this information to hydrogenation reactivity/selectivity, we pose a challenge to the catalysis community to synthesize metal nanoparticles with trace amounts of an active element in order to generate single atom alloy surfaces capable of similar efficient and selective hydrogenation chemistry.

Model Catalysts by Size-Selected Cluster Deposition

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We have made significant progress in three new research areas and are still extracting additional information in from the Pdn/TiO_2 system that we finished experiments on last year. One new area, undertaken with permission from the program manager, is electrochemical oxygen reduction over size-selected Ptn/glassy carbon electrodes. This was done by a DOE-funded graduate student and a postdoctoral fellow who came with support from the Deutsche Forshungsgemeinschaft. We constructed a cell with ~4 microliter volume that can clamp over the deposited cluster spot, when the sample is lowered into a sealed antechamber attached to the deposition ultra-high vacuum system. Linear sweep voltammetry and cyclic voltammetry experiments were carried out on a series of electrodes, including glassy carbon alone, and glassy carbon with Ptn (n = 1 – 10) deposited as size-selected clusters. We found that we were able to see some size effects, particularly in the linear sweep experiments; however, we also realized that the seal to the sample surface needs to be redesigned to eliminate a large resistive signal that results from electrochemistry occurring in a thin boundary layer that extends part way underneath the seal. We recently successfully tested a modified seal in the experimental vacuum chamber, which was moved to the benchtop for these tests. We are repeating the size-selected electrochemistry experiments ex-situ with the new electrochemical sell, and will return the electrochemistry chamber to the deposition machine to repeat the measurements in-situ as soon as we are confident that the problem is really solved.

We are currently looking at Pdn oxidation, and CO oxidation by Pdn deposited on an alumina film grown on a Ta single crystal. This work follows up on some interesting results we obtained for Pd oxidation as a function of cluster size for Pdn deposited on a bi-layer alumina film grown on NiAl(110). In that system, we were able to observe size-dependent shifts in the Pd XPS, indicating that different size clusters had different tendencies to oxidize upon exposure to O_2. Unfortunately, we were not able to do catalytic chemistry on the alumina/NiAl(110) surface, because the alumina film is so thin that oxygen spills over from the Pd to the surface, penetrates the alumina layer, and is effectively unavailable to participate in oxidation of adsorbates on the surface. For the thicker alumina films we are now growing (~2 nm), this effect does not seem to be a problem. Substantial signals for CO oxidation are observed, and we are in the process of working through the size dependence. We will be doing both UPS and XPS in conjunction with these studies to look at the relationship between valence and core electronic structure, and their effects on chemistry.

The final new system is hydrogen storage by Mg films, catalyzed by size-selected Pd (and eventually Pt and possibly other metal) clusters. We have run through this entire experiment, developing appropriate experimental protocols, using Pd/MgOx/Mg/Mo(100) samples grown by depositing and partially oxidizing a thick Mg film, then evaporating Pd to make the catalyst. These experiments were done in our 2nd UHV chamber, donated by Kodak, and gradually converted into a useful surface chemistry instrument over the past few years. This hydrogen storage project is next in the queue for time on the cluster deposition instrument.

Finally, we have continued to extract information from the massive amount of data collected in conjunction with CO oxidation experiments over size-selected Pdn/TiO_2(110). Recently, we have focused on understanding what happens on the sample during CO oxidation, in addition to the oxidation itself. We have a paper under review on the nature of the CO binding sites on these samples, and another nearly ready for submission that addresses processes such as oxygen spillover to the TiO_2, and encapsulation of the Pdn in TiOx under reducing conditions at high temperatures.

Spectroscopy of Organometallic Radicals

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In this project, we measure the 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 reactions. We seek to obtain accurate and precise information that can be used to establish what level of approximation is sufficient for accurate quantum chemical calculations on these complicated species. During the last year we have published papers on the spectroscopy of ZrF and OsN, and are currently working to record rotationally resolved spectra of CuCCH. Analysis of the spectrum of CrCCH is continuing, and soon we will begin work on the spectroscopy of UN, NUN, ThC, and ThO_2, which are of interest to us because of the great difficulties in calculating the properties of actinide compounds. Another important part of this project is the construction of a 22-pole cryogenic ion trap for ion photodissociation studies. This project is proceeding slowly because of its intrinsic complexity, but we have now succeeded in creating an intense beam of mass-selected ions, and are now working to trap them efficiently.

Results on ZrF show that the molecule has a ground state with OMEGA=3/2, and with a bond length of re = 1.854(1) Å. It is thought that the ground state is a 2DELTA3/2 level deriving from the 3sigma2 1delta1 configuration, but the possibility that it is a 4PHI3/2 term arising from a 3sigma1 1delta1 2pi1 configuration cannot be rigorously excluded.

Our study of OsN confirmed that the ground state is 2DELTA5/2, and establishes the ground electronic configuration as 1delta3 3sigma2, with a bond length of r0= 1.62042(6) Å. The most important contribution from this work, is the identification of three 2PHI7/2 and four 2PI3/2 excited states arising from the 1delta3 3sigma1 2pi1 and 1delta2 3sigma2 2pi1 electronic configurations. Our observation and detailed characterization of these states presents a challenge to computational chemists who seek to develop methods to properly treat the excited states of these complicated systems.

Our study of CrCCH has established that the ground state is of 6SIGMA+ symmetry, and the observed excited state is also a 6SIGMA+ state. We are still working to fully analyze the spectra of this linear molecule.

Thermochemistry and Reactivity of Transition Metal Clusters and Their Oxides

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The objectives of this project are to obtain quantitative information regarding the thermodynamic properties of transition metal clusters, their binding energies to various ligands, and their reactivities. This is achieved by using a metal cluster guided ion beam tandem mass spectrometer (GIBMS) to measure absolute cross sections as a function of kinetic energy for reactions of size-specific transition metal cluster ions with simple molecules. Analysis of the kinetic energy dependent cross sections reveals quantitative thermodynamic information as well as kinetic and dynamic information regarding the reactions under study.

Hydration Mechanisms in Nanoparticle Interaction and Surface Energetics

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Emerging nanoparticle technologies require new techniques to control surface properties of the 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. 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. The present 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. Recent results include predictions of surface thermodynamics on functionalized heterogeneous and ionized surfaces, and electric control of wetting by electrolyte solutions. 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. Theoretical studies of the new effects we anticipate to uncover will likely inspire future experiments. They 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.

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

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An important development in nanoscience is the possibility of designing nanoscale materials with chosen atomic clusters as the building blocks. Since the properties of small clusters are found to change with size and composition, such an approach offers the promise of making materials with selected properties. Our current DOE program proposes to undertake a comprehensive approach starting from electronic structure calculations and magnetic properties of free clusters for identifying stable magnetic motifs of varying band gaps, to investigation of the transport properties of molecules of such motifs, and explore synthesis and properties of larger assemblies of such motifs. The program involves four interrelated areas of study: (1) extention of 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, Ag, and Au atoms; (2) studies of ligated clusters containing transition metal atoms and clusters coated with Ag or Au and ligated with thiolate and other ligands following our recent work on MnAu24(SH)18; (3) studies of silicon transition metal clusters to find stable magnetic motifs containing multiple transition metal and silicon atoms; and (4) development of 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 collaborations with experimental groups involved in synthesizing nanoassemblies using synthetic chemical methods, we will work with experimental groups to form similar assemblies of magnetic superatoms. The research promises a new class of nanoscale materials with potential applications in spintronics and other areas.

Correlating Electronic and Nuclear Motions During Photoinduced Charge Transfer Processes using Multidimensional Femtosecond Spectroscopies...

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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 electron transfer.

Over the past 1.5 years, our work has focused on the following areas: (1) understanding photoinduced linkage isomerism in Fe(II) complexes, (2) 2D IR spectroscopy of mixed valence complexes to measure vibrational couplings between terminal and bridging cyanide ligands, (3) elucidating the role of high frequency vibrations during ultrafast back electron transfer, (4) developing fifth-order spectroscopies to measure the non-equilibrium spectral density of metal-cyanide stretching frequencies during a photoinduced electron transfer process, (5) using DFT based methods to model Fe K-edge transient x-ray experiments probing ultrafast photoinduced spin crossover in Fe(II) complexes, and (6) using the Ru L-edge x-ray spectrum as a probe of electronic changes during intramolecular charge transfer processes.

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

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The environmental impact of carbon dioxide and carbon monoxide has been a hot topic in the literature for decades. One area of highly active research in this field focuses on the development of solutions to removing carbon dioxide from what is pumped into the atmosphere in general during industrial processes.

Of the many methods available to “scrub” carbon dioxide from industrial emissions, most result in the capturing of the pollutant in some way for disposal by landfill or by dumping into the sea- a temporary solution at best. Compounding this issue is the fact that current technologies available for carbon dioxide capture from flue gas or other point sources are either highly expensive to implement or have very low efficiency- such as chemical absorption, permeation though membranes or cryogenic distillation.

A more viable solution is the reclamation of carbon dioxide and subsequently photocatalyze (chemically convert using light) to potentially usable products. Traditionally, semiconductors have been considered as ideal candidates for such a photcatalytic process. However, most traditional semiconductors for this application, such as titanium dioxide, require ultraviolet light in order to provide sufficient energy for carbon dioxide reduction reactions. A material requiring visible light would be more ideally suited for carbon dioxide conversion applications.

Porous coordinated polymers (PCPs) can be tuned for selectivity of carbon dioxide. Additionally, catalytic sites can be integrated into the porous framework and a carbon dioxide redox potential can be engineered by choosing the appropriate combinations of organic linkers. Organic linkers can be made so that PCPs utilize visible light energy to photo-chemically convert carbon dioxide.

The sheer number of possible configurations and elements is huge. Using cutting-edge ab-initio and empirical techniques, we computationally (1) design and construct photoactive PCPs that selectively adsorb carbon dioxide as well as fundamentally understand their chemisorption/physisorption properties, (2) determine chemical reaction barriers of carbon dioxide conversion to other usable products within confined PCP geometries, and (3) understand the charge transfer mechanisms in photocatalytic PCPs by developing a practical massively-parallel code for molecular-dynamics simulations allowing for quantum (electronic) transitions.

In our proposed research project, we study candidate PCP structures from the literature to determine their photoactive properties, their carbon dioxide selectivity and their photocatalytic properties using a variety of both statistical and ab-initio methods that are uniquely powerful when used in combination with one another.

Quantum Monte Carlo Calculations of Chemical Binding and Reactions

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The goal of this project is to apply the auxiliary-field quantum Monte Carlo (AFQMC) method so as to reliably predict binding strengths and reaction pathways of nano-structured materials, which is critical to the design of optimized properties for energy management.

The phaseless AFQMC method, recently developed by the PIs, is an orbital-based many-body approach, which can be expressed with respect to any single-particle basis (e.g., Gaussians, planewaves, Wannier, etc.). Gaussian type basis functions have played a crucial role in theoretical quantum chemistry, since they provide a compact and efficient representation of the wave functions in molecules and nanoscale systems. With Gaussian basis sets, AFQMC treats the same Hamiltonian as that of a corresponding quantum chemistry many-body calculation, allowing, for example, direct comparison of absolute total energies in molecules. The PIs have shown that compared to coupled-cluster CCSD(T), the preeminent many-body quantum chemistry method, the accuracy of AFQMC is similar to near equilibrium geometries and better when bonds are stretched. Because AFQMC exhibits much better scaling than standard quantum chemistry approaches, it provides new opportunities for efficient and accurate many-body calculations of ground and excited states.

The development of the AFQMC method with Gaussian basis sets has reached a tipping point. Major applications are now within reach. To achieve this potential, AFQMC needs new algorithmic improvements, incorporating techniques from standard quantum chemistry methods, which exploit the analytic properties of Gaussian basis sets. AFQMC has a close formal resemblance to a mean-field density functional theory (DFT) or Hartree-Fock (HF) calculation, taking the form of an entangled ensemble of mean-field calculations in fluctuating external fields. Thus, many efficient techniques developed for DFT and HF can be directly imported. This was done by the PI’s with planewaves where tremendous speed-ups were achieved.

The project will first be focused on building this computational infrastructure. We will implement quantum chemistry techniques such as resolution of the identity methods and linear scaling of exchange-type integrals. The favorable computational scaling of the AFQMC method with system size and its exceptional potential for parallel scaling will be exploited to effectively use large-scale computing platforms. Then as our first application we will carry out calculations of the functionalization of graphene-based and related systems, where standard methods based on DFT are known to be deficient.

The development of this theoretical capability will have cross-cutting impacts beyond specific systems, extending to strongly correlated transition metal oxides and materials containing 4f- and 5f-electron elements. The techniques and codes we will develop are very general and applicable to many other materials problems. By establishing highly accurate benchmark calculations, the results will validate less computer intensive methods. The capability of these tools will allow a new level of prediction and understanding of nano-structured materials.

Modeling Carbon Dioxide Capture and Separation in Zeolitic Imidazolate Frameworks

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The research objectives of the present work are to understand the microscopic origins of the properties of zeolitic imidazolate frameworks (ZIFs), nanoporous metal-organic framework (MOF) compounds consisting of Zn^{2+} cations and organic imidazolate linker groups. We are focusing primarily on those properties of relevance to CO_2 capture and flue gas separation, elucidating the microscopic interactions between CO_2 and the ZIF using quantitatively-accurate first-principles techniques; these will further allow us to decompose this interaction into it constituent physical components (electrostatic, polarization, Pauli repulsion, dispersion, etc.)

We are utilizing symmetry adapted perturbation theory (SAPT) to construct force-fields tailored to study CO_2 adsorption in nanoporous ZIFs. Our approach utilizes the SAPT energy decomposition to generate physically-motivated force fields for the CO_2-CO_2, N_2-N_2, and CO_2-ZIF interaction, with explicit terms representing exchange, electrostatic, induction and dispersion interactions. Each of these terms is fit to the corresponding term in the SAPT energy decomposition, yielding a force field entirely free of empirical parameters. Due to the physical nature of their construction, these force fields are robust and transferable to environments for which they were not specifically parameterized. Furthermore, the explicit correspondence between force field terms and fundamental interaction types (dispersion, electrostatics, induction) allows for an analysis of the underlying physics controlling gas absorption that is not possible with the generic force fields that had been previously utilized to study these systems. As our force fields are free from empirical parameters, these results demonstrate the potential for computationally screening novel ZIFs for flue gas separation applications with near quantitative accuracy. Although we have focused specifically on the CO_2-ZIF system, we expect the general methodological approach, generating physically-motivated force fields via SAPT, to be widely applicable to a variety of complex systems ranging from gas adsorption to bio-molecular interactions.

We are also examining the possible role of common flue gas contaminants (water, NOx, SOx) with various MOFs, focusing specifically on those containing unsaturated metal centers. Here the under-coordinated metal strong binds a CO_2 molecule, leading to high uptake and thus excellent adsorption/separation properties. These same properties may also yield strong interactions with flue gas contaminants. We utilize quantum calculations to examine the binding strength of various contaminants with representative unsaturated MOFs, and employ simple statistical-mechanical models to estimate the implications of flue gas contaminants on the thermodynamics and dynamics of gas separation. We also consider the possible implications for such contaminants on framework stability.

Water Dynamics in Heterogeneous and Confined Environments: Salt Solutions, Reverse Micelles, and Lipid Multi-Bilayers

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PROJECT 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 are playing very important roles. We are developing techniques for calculating spectroscopic observables, and then using our results to analyze and interpret experiment.

RECENT PROGRESS

We have calculated nonlinear spectroscopic observables for bulk water, ice Ih, the water liquid/vapor interface, water in salt solutions, water in reverse micelles, and water in lipid multi-bilayers. In all cases we compare with existing experiments if possible. We find that the structure and dynamics of water are very sensitive to its local environment.

FUTURE PLANS

In addition to continuing on in the above areas, we plan to expand our scope to several news topics, including Raman spectroscopy of supercritical water, pump-probe and 2DIR spectroscopy of ice Ih, 2DSFG spectroscopy of the water liquid/vapor interface, SFG spectroscopy of water near the headgroups of lipid monolayers, and the vibrational spectroscopy of urea/water mixtures.

The Role of Electronic Excitations on Chemical Reaction Dynamics at Metal, Semiconductor, and Nanoparticle Surfaces

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Achieving enhanced control of the rates and molecular pathways of chemical reactions at the surfaces of metals, semiconductors, and nanoparticles will have an 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.

Understanding the Electron-Water Interaction at the Molecular Level: Integrating Theory and Experiment in the Cluster Regime

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Funding:	$105,000

We are building predictive, “bottom-up” models that accurately describe aqueous processes at the molecular level. The key to our approach is to characterize sufficiently representative model systems isolated in the gas phase and the many factors necessary to recover the complex, cooperative effects in solution that are explicitly manifested in microscopic observables. These microscopic model systems are important because they can be treated with accurate theoretical methods as “supermolecules,” thus allowing a detailed description of both reactive encounters as well as the speciation of reactive intermediates important in radiation chemistry. This includes structural characterization of water networks that bind excess electrons in order to unravel how the topology of a network controls excess electron localization and radical anion formation. This aspect of the work has led to a microscopic picture of the hydrated electron, a key reactive intermediate in aqueous radiation chemistry.

An important component of this endeavor is the application of novel model Hamiltonian approaches to explore the potential energy surfaces of the micro-solvated anions. These calculations explore the topology of the complex potential surface describing reactions in solution, and are benchmarked by direct measurement of the photoinduced interconversion between different shapes of solvent networks. We have most recently focused on the critical reaction intermediates that occur in the activation of carbon dioxide in its photoelectrochemical conversion to fuel. In particular, we have isolated the formation of the critical C-N bond formation step in reductive activation with a pyridine catalyst, and further followed how water networks mediate electron attachment to the neutral molecule in the first steps of the formation of the radical anion. One surprising result from our work on reductive activation is that the formate ion, a common intermediate in the conversion of carbon dioxide, has a very dramatic change in structure upon solvation. We traced this behavior to strong vibronic interactions (i.e., molecular geometry dependence of the electronic wavefunction) that occur upon hydrogen atom attachment to the carbon dioxide anion in the formation of the C-H bond.

DOE National Laboratories

Chemical Physics - Base Program

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Funding: $355,000

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.

The other major effort involves statistical mechanical and multiscale modeling 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 multiscale 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."

Theoretical and Computational Tools for Modeling of Energy Relevant Catalysis on Multiple Scales

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Funding:	$125,000

The goal of this research is to enable the achievement of highly scalable multi-scale modeling of catalytic processes related to energy needs. The DOE BES Report describing "Basic Research Needs in 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 from both biomass conversion and from more traditional feedstocks. The report noted the critical role of theory, computation, and simulation in providing the molecular-level understanding necessary to address these challenges.

With regard to the first Grand Challenge listed, advances in high-level electronic structure methods, including novel hybrid multi-level approaches, are clearly critical for elucidating reaction mechanisms and dynamics in complex environments. In addition, a description of the overall (macroscopic) catalytic reaction process requires coupling to either mean-field type microkinetic modeling or, preferably, to higher-level atomistic statistical mechanical modeling. However, existing molecular-level modeling which reliably describes the overall reaction processes is very limited. With regard to the second Grand Challenge listed, there has been relatively little high-level modeling of the formation, stability, and structure of catalyst materials and nanostructures in the chemical physics community. Thus, our research involves the development of and new strategies for integrated combinations of electronic structure analysis and statistical mechanical and coarse-grained modeling approaches. Essential to these efforts is the development of novel new approaches in not only theoretical chemistry and materials science (BES), but also computational science and applied mathematics (ASCR).

The targeted catalytic materials to be described by these new modeling tools include extended and mesoporous oxide surfaces, as well as metal surfaces and supported nanostructures. Of particular interest are energy-relevant catalytic reaction processes that address biomass conversion utilizing mesoporous silica and carbon nanoparticles, and reactions catalyzed by metal surfaces including supported nanoclusters. We are also working to address the evolution under reaction conditions of metal surfaces and of supported metal nanoclusters. Here, issues related to formation and stability are critical. For the description of both catalytic reaction kinetics and catalyst structure, high-level electronic structure calculations will provide critical guidance on the energetics for the statistical mechanical or coarse-grained modeling of the overall process."

Single Molecule Chemical Imaging at Femtosecond Time Scales

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Funding:	$558,000

Understanding energy transfer dynamics at nanometer length and ultrafast time scales in molecular and material systems is well-aligned with the DOE BESAC Grand Challenges. In particular, energy transfer is at the heart of photovoltaic, photosynthetic, and catalytic processes that are critical to energy generation and conversion. Towards this end, we propose an advanced experimental approach that integrates UHV STM and single particle resonant laser spectroscopy such that energy transfer and charge separation from photoexcited excitons can be probed with atomic-scale spatial resolution and ultrafast time scales. We will apply this strategy to an array of systems with direct relevance to developing technologies, including single molecules on transparent conductors; layered organic, inorganic, and hybrid structures; and covalently linked donor-bridge-acceptor (DBA) molecular systems. The transfer of energy from a photoexcited exciton to an electrical potential proceeds through several stages: (1) photon absorption, (2) exciton migration to the acceptor-donor interface, (3) charge separation, and (4) charge migration to electrodes or a catalytic site. These processes span femtoseconds to microseconds and occur at nanoscale interfaces, either between donor-bridge-acceptor complexes, donor-acceptor layered structures, or photoactive material-electrode interfaces. The goal of this project is to elucidate these fundamental energy transfer processes and thus provide guidance to the development of future photovoltaic technologies. Ultimately, we envision a nanoscale photovoltaic device in which the photoexcited charges are extracted with the STM tip, which serves as a sub-nanometer back electrode.

Theoretical/Computational Studies of the Fundamentals of One-Component and Alloy Metal Based Nanocatalysis Relevant to Alternative Sources of Energy

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Funding:	$131,000

The focus of this program is theoretical/computational studies aimed at advancing our fundamental understanding of one-component and alloy metal based nanocatalysis relevant to alternative sources of energy. The emphasis is on unraveling and characterizing the separate and combined roles of the structural and electronic features of metal nanocatalysts and the key dynamical mechanisms that underlie their activity and selectivity. These are investigated as a function of the catalyst particles' size and composition (both elemental and percentile) as well as the material of the supports. Among the primary targets are catalysts and reactions relevant to conversion of lower hydrocarbons into alternative liquid fuels. The understanding and knowledge we expect to gain will benefit the broad field of catalysis in general.

Surface Chemical Dynamics

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Funding:	$1,075,000

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 down to subpicosecond timescales and are used to infer the dynamics of adsorbate–substrate energy transfer. A new effort to investigate the electronic structure and time-resolved dynamics of metal and semiconductor nanoclusters supported on metal oxide surfaces using two-photon photoemission has also been initiated. A unique aspect of this work is the use of a cluster ion beam apparatus to deposit size-selected metal and metal compound clusters. In addition, we are extending our current time-resolved reaction studies to investigations of nanoscale confinement effects in chemistry by measuring the size-dependence of photoinduced desorption of molecules from the surface of supported metal nanoparticles.

Condensed Phase and Interfacial Molecular Science

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Students:	3 Postdoctoral Fellow(s), 5 Graduate(s), 0 Undergraduate(s)
Funding:	$1,230,000

The behavior of ions, electrons, and radicals in solutions and especially near interfaces is examined with state-of-the-art methods of theory and experiment. Interfacial charge transport is probed with femtosecond two photon photoemission (2PPE), specifically addressing electrochemical interfaces and ionic liquid systems. The electronic structure of pure liquids and solutions and their surfaces is examined with soft synchrotron x-ray spectroscopy, enabled by novel liquid microjet technology, and complimented by new theoretical methods being developed at Lawrence Berkley National Laboratory. A detailed molecular description of liquid evaporation is sought via laser and mass spectroscopic studies of liquid microjets in combination with transition path sampling methods. Path sampling of classical and quantal models is used to study dynamics of hydrated ions at metal and nanoscale interfaces. Simulation methods are used to examine electron transfer and proton transfer processes in catalytic and photovoltaic systems. 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. In all of this work, emphasis is on the study of aqueous systems of relevance to energy conversion applications and on surface chemistry relevant to combustion.

Chemical Kinetics and Dynamics at Interfaces

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Funding:	$3,228,000

The Condensed Phase Chemical Physics Program supports the mission of the DOE Office of Basic Energy Sciences to foster and support fundamental research in the natural sciences to provide a basis for new and improved energy technologies (e.g., catalysis and energy conversion) and for understanding and mitigating the environmental impacts of energy use. This research provides a foundation for understanding fundamental interactions of atoms, molecules, and ions with materials and with photons and electrons in their chemical environment. Research underpins the fundamental knowledge of chemical transport and reactivity in the condensed phase. It also addresses fundamental uncertainties in thermal and non-thermal (i.e., radiation) chemistry, interfacial molecular and ionic transport (key to subsurface contaminant transport and to separations processes), and other processes in complex systems related to energy use, environmental remediation, and waste management. Our research focuses on structures and processes of molecular and nanoscale systems in complex environments such as condensed phases and interfaces. Experimental and theoretical models are used to better understand natural systems and guide the development of new materials and approaches for clean and efficient energy use. Another central feature is the development of new experimental methods with broad applications to research in the natural sciences.

Molecular Theory and Modeling

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Funding: $2,150,000

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.

Fluctuating Conformations and Local Chemical Environments of Macromolecules Studied Using Time-Resolved, Multispectral Single Molecule Imaging

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Funding: $600,000

The unique chemical functions of macromolecules, such as proteins, largely arise from their ability to create distinct local chemical environments, such as binding sites. The complex conformations and chemical compositions of macromolecules produce diverse and highly specific functions. Conformational fluctuations play an important role in macromolecule functions because they change the accessibility and nature of chemically reactive sites. In this research project we study the fluctuations in the conformations and local chemical environments of macromolecules using simultaneous, time-resolved measurements of multiple fluorescence properties of probe fluorophores in single macromolecules. Our approach combines unique capabilities to measure the properties of each detected fluorescence photon with rigorous new data analysis methods that extract the maximum information about the macromolecule fluctuations from the experimental record of photons. The goal of this research is to understand the relationship between conformational fluctuations and function in macromolecules. During this proposal period, we focus on single-molecule methods applied to the study of conformational fluctuations of ligand binding proteins and DNA aptamers. We also begin to investigate effects on conformation and reactivity of interactions between macromolecules and materials such as lipid membranes. While our experiments focus on studies of macromolecule dynamics, the chemical-environment-sensitive imaging techniques being developed also impact studies in other areas where nanoscale chemical reactivity is important.

Gas-Phase Chemical Physics

Institutions Receiving Grants

Dynamics of Large Amplitude Motion in Energized Molecules

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Funding:	$122,000

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 those of current engines and 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 will evaluate one of the underlying assumptions of reaction rate theories. All chemical reactions, by their nature, involve large-amplitude motion of the nuclei; and most theories of reaction rates invoke a separation of variables between the large-amplitude (i.e., reactive) motion and the other small-amplitude vibrations. The proposed work will evaluate the limits of validity of approximate separations of the nuclear degrees of freedom and explore the nature of the couplings between degrees of freedom.

This project will probe the dynamics that result from the coupling between nuclear degrees of freedom in molecular systems with two (or more) large amplitude degrees of freedom. In order to access the precision and detail available from high-resolution spectroscopy, large-amplitude degrees of freedom in bound molecular systems will be 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. When the infrared bright state is in resonance with a “doorway” state, coupling into the bath of torsional combination states occurs and is revealed by intensity borrowing from the bright state. Model calculations will be used to interpret the molecular dynamics revealed by the spectra and look for systematic trends across related molecular systems. Other large-amplitude systems to be investigated include acetylene, tropolone, and the hydrogen trioxy radical. This project will provide an understanding of when approximate separations of degrees of freedom are valid and when two-dimensional or higher treatments are essential.

Three different experimental approaches will be employed:

(1) In collaboration with the Pate group at the University of Virginia, a coherence-converted population transfer Fourier transform microwave – infrared spectroscopy will be used to obtain rotationally state-selected infrared spectra.

(2) In our Akron lab, a slit-jet in combination with continuous-wave infrared lasers, and cavity ringdown detection to obtain sub-Doppler infrared spectra with high sensitivity will be used.

(3) In collaboration with Ilana Bar at Ben Gurion University in Israel, a low-resolution overtone spectra of both gas phase and jet-cooled molecules will be obtained.

In the case of acetylene, no new spectra will be recorded; and the spectroscopic Hamiltonian developed by Michel Herman of the Université Libre de Bruxelles in Belgium will be used to evaluate the stability of the local bender as a potential reaction coordinate to vinylidene.

Probing Chemical Dynamics by Structurally Sensitive Photoionization

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Funding:	$145,000

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 that unfold 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, provides very clear spectral signatures of molecular structures. Among the many unique attributes of this technique are that 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. Amongst 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.

Modeling Reactions in High-Pressure Turbulence in the Cold Ignition Regime

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Funding:	$125,000

This study is devoted to investigating the coupling among chemical reactions, thermodynamics, turbulence and transport properties in the cold ignition, high-pressure regime. Both experimental data and Direct Numerical Simulation (DNS) conducted in high-pressure environments akin to those in the cold-ignition regime, show that species mixing yields a highly inhomogeneous flow with numerous convoluted high density-gradient magnitude (HDGM) regions; the simulations indicate these to be the coupled result of the distortion of the original density boundary between fuel and carrier gas and of species molecular mixing. The HDGM regions redistribute turbulent energy from their normal to their tangential direction and are the site of species mixing impeded by mixture non-ideality. Reactions occurring in such an environment are thus dominated by the molecular mixing time rather than the chemical kinetic time.

It is here proposed to create a DNS database of a reacting flow under high-pressure turbulence to examine and understand the chemical-reactions/thermodynamics/turbulence/transport-properties coupling. The DNS database will be created by solving the mass, momentum, species and total energy conservation equations coupled to a real-gas equation of state. The species flux and heat flux in the conservation equations will include Soret and Dufour effects, respectively, and the transport properties will be functions of the thermodynamic variables. The database will encompass realizations obtained by varying different initial parameters. This database will be analyzed a priori to examine the chemical-reactions/thermodynamics/turbulence/transport-properties coupling and develop subgrid-scale (SGS) models for Large Eddy Simulation (LES). These SGS models will describe (1) viscous, species and enthalpy SGS fluxes, (2) unresolved reaction source terms, and (3) any LES assumption (i.e., the statement that a filtered quantity in a conservation equation is equal to the quantity computed from the filtered flow field) found to be not satisfied when assessed according to a specified norm. A posteriori study will be conducted to evaluate the capability of these SGS models to reproduce the chemical-reactions/thermodynamics/turbulence/transport-properties coupling by comparing LES predictions with the filtered DNS data at the LES scale. These comparisons will particularly include the scalar dissipation. Finally, LES will be performed at the same conditions as those for which there is ignition delay time experimental data to further assess the quantitative predictive capabilities of the developed models.

Determination of Accurate Energetic and Spectroscopic Database for Combustion Radicals and Molecules by High Resolution Photoion-Photoelectron Methods

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Funding:	$146,000

The main goal of this research program is to obtain accurate thermochemical and spectroscopic data, such as ionization energies (IEs), 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 (PIE), pulsed filed ionization-photoelectron (PFI-PE), and PFI-photoion (PFI-PI) 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 been demonstrated to be a very sensitive method for high-resolution IR spectroscopic measurements of polyatomic species. A high-resolution VUV threshold photoelectron-imaging (VUV-TPEI) technique has been shown to achieve an energy resolution of 2 cm-1 (FWHM). The high sensitivity of the VUV-TPEI 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 (n-C_4H_3), 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 ion-imaging 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 (VUV-RT-TOF) techniques developed in our laboratory will be employed in the photodissociation studies. In addition to the experimental projects, we also plan to continue with high-level ab initio quantum calculations for comparison with experimental results and guiding experimental measurements.

Dynamics and Energetics of Elementary Combustion Reactions and Transient Species

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Funding:	$200,000

This research program examines the energetics and dynamics of transient neutral species and collision complexes relevant to combustion phenomena. In the current year, we have made important advances in the characterization of the structure, energetics and dynamics of the elusive combustion intermediate HOCO in particular. The experimental approach used in these studies involves measurement of the photodetachment and dissociative photodetachment (DPD) of negative ion precursors of important neutral combustion intermediates using photoelectron-photofragment coincidence (PPC) spectroscopy, a technique developed in this laboratory in the 1990's. This year we have exploited a new cryogenic electrostatic ion beam trap (CEIBT) to study the photoelectron spectra and examine DPD processes on cooled anion precursors for the first time. This new PPC spectrometer is capable of a whole new generation of experiments with the trap installed. Both the sensitivity and resolution of the new trap are higher than the old single-pass configuration of the spectrometer. Using the CEIBT we have carried out studies of the decomposition of HOCO/DOCO to H/D + carbon dioxide via tunneling, allowing experimental extraction of the barrier to carbon dioxide production.

High-resolution photoelectron spectroscopy measurements have also been performed on HOCO- and DOCO- at a number of wavelengths, providing accurate values for the electron affinities for both cis- and trans- isomers of HOCO. Three new vibrational frequencies have been determined for both isomers of HOCO and DOCO in collaboration with theoretical studies by John Stanton at UT Austin. These findings will be of value to researchers seeking to detect HOCO in combustion and atmospheric chemistry environments. Beyond these results, we examined the dissociation dynamics of nitric oxide – water complexes, revealing a strong coupling of NO vibration with the dissociation coordinate in the strongly interacting cluster. Studies of the dissociation of the tert-butoxy and ethoxy radicals are also on-going, as well as an isomer of HOCO, the formyloxyl radical, HCO_2. We have also assembled a tunable IR laser system that will allow selective excitation of vibrational modes in precursor anions and determine the impact of vibrational excitation on the radical dissociation processes in a controlled manner. All of these efforts support our overall goal of determination of the energetics and reaction dynamics of important combustion intermediates, allowing more quantitative evaluation of their roles in combustion and validation of theoretical approaches to predicting the dynamics of combustion reactions.

Dynamics of Product Branching in Elementary Combustion Reactions

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Funding:	$164,000

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. The reaction rate and the branching to multiple product channels can evidence a strong temperature and pressure dependence. While the total rate constant for many elementary reactions is well-characterized, understanding the product branching in complex reactions presents a formidable challenge. For example, in the reaction of OH with alkenes, though many combustion mechanisms only include the H-atom abstraction channel, the addition mechanism can lead to several competing product channels. To gain an incisive probe of such reactions, our experiments use molecular beam scattering and velocity map imaging experiments to directly probe the intermediate dynamics of the product channels that arise from vibrationally-excited radical intermediates. Our experiments generate a particular isomeric form of an unstable radical intermediate along a bimolecular reaction coordinate, characterize its vibrational energy distribution, and investigate the branching between the ensuing product channels of the energized radical as a function of its internal energy under collision-less conditions. They probe the reaction from each radical intermediate to the competing product channels and determine the energetic barriers in both the entrance and the product channels. The experimental results offer a direct test of product branching calculated from theoretical predictions of the microcanonical rates, k(E), of each product channel relative to the other competing product channels resulting from an addition mechanism. Recent results include those on the OH + ethene reaction and the reaction of O atoms with allyl radicals, with ongoing work on the OH + propene and OH + allene reaction.

Spectroscopy, Kinetics, and Dynamics of Combustion Radicals

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Funding:	$149,000

Spectroscopy, kinetics and dynamics of jet cooled hydrocarbon transients relevant to the DOE combustion mission have been explored, taking synergistic advantage of (1) high resolution IR lasers, (2) slit discharge sources for efficient production of supersonically cold radicals, and (3) long path length detection with direct absorption sensitivities (10^-7/Hz^1/2) near the quantum shot noise limit (10^7 radicals/cm^3/quantum state). With such a hybrid approach, targeted radical transients can be "synthesized" by electron dissociative attachment with commercially available alkyl halide precursors. This yields remarkably high concentrations (under favorable conditions up to 10^16 radials/cm^3) at pressures characteristic of combustion conditions, and yet rapidly cools the radicals (T = 10-20K) into a small number of quantum states in slit supersonic expansion environment. In conjunction with the powerful generality of tunable IR laser absorption methods over the 3-10 micron fingerprint region, this unique approach offers prospects for first time spectral study of many critical combustion species.

Atomic Scale Imaging of the Electronic Structure and Chemistry of Graphene and Graphite

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Funding:	$160,000

Our work is focused on fundamental chemical events taking place on carbon surfaces with the intent of shedding light on their role in mediating the formation of polycyclic aromatic hydrocarbons (PAHs) from small molecular precursors and the growth of soot particles. Scanning tunneling microscopy (STM) is the main probe technique that we use to study the interfacial structure and chemistry of carbon mainly because of its ability to investigate surface structure and dynamics with molecular or even atomic resolution. Scanning tunneling spectroscopy (STS), which measures the local density of quantum states over a single atom, provides information about the electronic structure of surfaces, surface films, and surface adducts. For the past two years this effort has been focused on the chemical behavior of graphene (a single graphite carbon sheet). We have now mastered the necessary preparation techniques that allow us to form graphene on insulators (silicon dioxide and mica) and metals (cobalt and copper). When compared to graphite, graphene constitutes a better laboratory model for mimicking the behavior of soot. First, the surface of graphene is not stabilized by the presence of multiple carbon sheets; second, it is relatively easy to form graphene flakes of different size on the nanoscale. For these small flakes (which are close in size to small soot particles or large PAHs) quantum confinement of electrons in the delocalized graphene aromatic p orbitals produces significant variations in electronic structure with changes in the size and shape of the nano-flakes. We have already shown that graphene is more easily oxidized than graphite. In addition the mechanisms for the reaction of these two species with O_2 are quite distinct. In particular, single sheet graphene is etched even in the absence of pit defects or step edges. We have also successfully grown graphene on a copper foil using CH_4 and NH_3 as precursors, which leads to the incorporation of nitrogen atoms into the graphene lattice. This chemical system will provide an opportunity to test the importance of metal atoms in mediating the reactivity of graphene, and should give us some clues to the chemistry of soot particles. By using STM to monitor both N and C atom sites on the surface, we should be able to follow the oxidation chemistry with atomic resolution.

Bimolecular Dynamics of Combustion Reactions

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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 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 products, by Rydberg tagging time-of-flight (TOF) methods. Reactions currently under study range from those of polyatomic molecules such as phenyl (C_6H_5) radicals with unsaturated hydrocarbons, where multiple reaction pathways are anticipated, to simple three-atom reactions such as $H + O_2 \rightarrow OH + O$ where high-level theory can be employed to predict product rovibrational energy distributions as a function of product scattering angle.

Investigation of Non-Premixed Turbulent Combustion

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The focus of the current work is on the development of computational approaches which allow our detailed knowledge of the chemical kinetics of combustion to be applied to the modeling and simulation of combustion devices. In the past year, the work has been focused on combining strategies for the accurate and efficient implementation of combustion chemistry in modeling and simulation of turbulent combustion. The methodologies used are (1) rate-controlled constrained equilibrium (RCCE) for the dimension-reduction of the combustion chemistry, (2) a greedy algorithm with local improvement (GALI) for the selection of good constrained species, and (3) in situ adaptive tabulation (ISAT).

We have developed a new methodology based on the combination of dimension reduction (using RCCE) and tabulation (using ISAT). In this combined approach, a specified set of represented (constrained) species is used as constraints to perform dimension-reduction. The specification of good constraints is crucial for the accuracy of dimension-reduction, and we have recently developed a new automated GALI for selecting good represented species.

The combined methodology has been extensively tested using the partially-stirred reactor (PaSR) for the methane/air premixed combustion. Based on these results, the following conclusions can be drawn about the ISAT-RCCE-GALI methodology: (1) it achieves the same level of accuracy as the detailed and reduced mechanisms with relatively fewer represented species; (2) it is computationally efficient, providing significant speedup relative to the detailed mechanism; and (3) it reduces the total number of scalars that need be carried in reactive flow simulations.

In current work, this combined methodology is being applied in large-eddy simulation (LES) probability density function (PDF) calculations of turbulent flames, using up to 9,000 cores.

Theoretical Studies of Combustion Dynamics

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Funding: $130,000

The project centers on two aspects of theory and computation. The first is the development of high-level ab initio-based potential energy surfaces to describe chemical reactions of relevance to gas-phase combustion. The second is performing dynamics calculations on the potentials to obtain detailed information about the branching ratio of products and their internal energy distributions.

Recent work has included the elucidation of so called “roaming” pathways in unimolecular dissociation. These novel pathways by-pass the conventional transition-state bottleneck to molecular products and instead visit regions of incipient radical formation. The experimental signatures of these pathways have been determined in collaboration with the theoretical work and typically consist of one molecular product being formed with a very high degree of internal excitation.

Other recent work has been on reactive and non-reactive quenching of OH^- by H_2, stimulated by outstanding experimental work of the group of Marsha Lester (Penn). We have made excellent progress on this very complex reaction, agreement with experiment is quite good, and predictions made by theory are stimulating further experiments.

Theoretical Studies of Chemical Reactions Related to the Formation and Growth of Polycyclic Aromatic Hydrocarbons and Molecular Properties of their Ke

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Because of the great environmental and health effects of polycyclic aromatic hydrocarbons (PAH) and their importance in different applications of combustion technology, there is a strong need for better understanding of the reaction pathways leading to ecologically hazardous PAH and soot in combustion flames. Chemical mechanisms of PAH formation and growth are complex, as the critical elementary reactions are convoluted and involve multiple interconnected isomers as products and/or intermediates. To understand, describe, and model these reactions in combustion engines, one needs to establish their energetics to determine rate constants, identify reaction products and their branching ratios under various conditions, and assign reaction intermediates. Complementary to experimental studies of these data, it is crucial to carefully investigate potential energy surfaces (PES) of these reactions.

In this project, we suggest to continue theoretical studies of the reactions of PAH formation and growth using highly-accurate ab initio molecular orbital (CCST(T)/CBS, G3, G4, and explicitly correlated methods) and density functional calculations of PESs and statistical (TST and RRKM/Master Equation) computations of absolute rate constants and product branching ratios. The underlying theme of the new 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. While phenyl has been long recognized as a critical intermediate in PAH growth, the appreciation of the role played by C5H5 has been growing in the last decade. Cyclopentadienyl radical is abundant in flames, and its ability to form naphthalene, indene, and larger molecules increases its sooting propensity. Therefore, any model wishing to address the problems of soot growth must capture the details of cyclopentadienyl's contribution to soot formation in addition to the other competing mechanisms. The theoretical studies of C_5H_5 and C_6H_5 reactions suggested in this project will represent an important step in this direction.

In addition, a variety of oxidation reactions competing with the PAH growth will be investigated. The list of reactions to be studied includes $C_5H_5 + C_4H_4$ and the $C_5H_5 + 2C_2H_2$ sequence, $C_5H_5 + O$, $C_5H_5 + C_5H_5$, $C_5H_5 + C_5H_6$, unimolecular dissociation of C_5H_5O (pyranyl) and C_5H_5-C_5H_4, $C_6H_5 + C_3H_6$, $C_6H_5 + C_4H_2$, $C_6H_5 + C_4H_4$, $C_6H_5 + C_4H_6$, $C_6H_5 + O_2$, and $C_{10}H_7 + O_2$. Our primary objectives are to (1) unravel reaction mechanisms through detailed, accurate, and reliable calculations of pertinent PESs; (2) 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; (3) 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, ionization energies and Fracnck-Condon factors, and electronic excitation energies and Franck-Condon factors.

The information derived from our theoretical studies of PESs and statistical calculations of absolute rate constants and product yields will not only bring a better fundamental understanding of mechanisms of chemical reactions in combustion, but will also provide important input for kinetic models describing complex reaction systems in combustion flames and, therefore, will be of great aid to improve the existing models of reaction networks for PAH formation and growth. In turn, the improvement of the models of these complex combustion systems will help researches and engineers to prevent or minimize PAH and soot formation, to develop cleaner combustion equipment, and thus to guarantee cleaner air conditions.

Theoretical Studies of Elementary Hydrocarbon Species and Their Reactions

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Funding:	$202,000

This research program carries out both methodological development and cutting-edge computational applications of first principles electronic structure theory, as directed toward the fundamental chemical physics underlying diverse problems in combustion chemistry. In order to build and refine the world's database of thermochemistry, spectroscopy, and chemical kinetics for hydrocarbon compounds, next-generation electronic structure methods are needed to achieve very high accuracy in theoretical predictions, requiring the ability to pinpoint relative energies to within 0.1-0.2 kcal/mol. Toward this ambitious goal, our work focuses on rigorous single- and multi-reference coupled cluster methods, executed to the level of triple or quadruple excitations and pushed to the complete basis set limit via new explicitly correlated R12 techniques or more established extrapolation schemes. Concerted effort has been made to develop open-shell wave function methods that can properly handle the free-radical chemistry predominant in combustion mechanisms. In addition to electronic structure methods of highest accuracy, another hallmark of this research is the incorporation of anharmonicity in treatments of molecular vibrations by means of variational or perturbative schemes applied to complete quartic force fields.

Representative chemical applications pursued in this research program are as follows:

(1) Reactions of alkyl radicals (R) with O_2 are ubiquitous in combustion, atmospheric chemistry, and biological processes. As the size of the alkyl radical grows, R + O_2 reactions rapidly become more complex, and isomerizations to hydroperoxyalkyl radicals (QOOH) can increase in importance relative to concerted elimination of HO_2. In a herculean investigation, we fully optimized geometries at the CCSD(T)/cc-pVTZ level of theory for all chemically relevant minima and transition states of the *n*-propyl and *i*-propyl + O_2 systems. For incorporation into chemical kinetic models, final energetics were derived from explicit computations with basis sets as large as cc-pV5Z and correlation treatments as extensive as coupled cluster through full triples with perturbative inclusion of quadruple excitations [CCSDT(Q)].

(2) Environmental, toxicological, technical, and fundamental scientific concerns continue to drive both experimental and theoretical research on soot formation during hydrocarbon combustion. Soot formation centers around the growth of polycyclic aromatic hydrocarbons (PAHs), some of which are carcinogenic and/or mutagenic. The best candidate PAH precursors are resonance stabilized free radicals (RSFRs), whose enhanced stability and resistance to attack by O_2 allow the buildup of significant populations of these species under typical flame conditions. Our recent work has systematically investigated the allyl + propargyl reaction system as an alternative to propargyl + progargyl for the production of aromatics in the combustion of aliphatic fuels. Ongoing research is targeting the recombination of the benzyl and propargyl RSFRs to generate two-ring aromatic hydrocarbons.

(3) Chemically balanced reactions such as isodesmic and homodesmotic transformations are often used for both interpretation and error cancellation in computational chemistry. In our recent comprehensive analysis, we set forth canonical and chemically insightful criteria in order to construct a new and

rigorous hierarchy of reaction classes (isogyric, isodesmic, hypohomodesmotic, homodesmotic, hyperhomodesmotic), with each type successively conserving larger groups of atoms. This hierarchy leads to a highly effective scheme for computing enthalpies of formation of larger hydrocarbons by means of generalized bond separation reactions, in which the target compound is uniquely decomposed into elemental molecular products via reactions with elemental molecular reactants. Computations of unprecedented size and accuracy are now being executed to pinpoint the enthalpies of formation of all elemental molecular reactants and products within our reaction classes, thus providing the benchmarks to sequentially compute the thermochemical database of combustion species well beyond the accuracy of existing experimental determinations.

(4) The hydroxycarbenes (R–C–OH, R = H, phenyl, methyl) are archetypical donor-substituted carbenes which have been implicated as key reactive intermediates in the high-energy chemistry of carbonyl compounds. Nonetheless, these species escaped isolation and direct spectroscopic characterization despite repeated efforts over many years. A synergy between our theoretical research and a German experimental group led to the first successful preparations of these hydroxycarbenes by means of high-vacuum flash pyrolysis (HVFP) followed by immediate matrix isolation. This achievement led to a surprising discovery that these hydroxycarbenes spontaneously disappear within a few hours by pure quantum mechanical tunneling under large barriers of about 30 kcal/mol, even at very low temperatures. The occurrence of such a tunneling event on a tangible time scale is an eye-opening chemical phenomenon with little precedent. Moreover, the methylhydroxycarbene cases demonstrate the need to consider *tunneling control* in addition to classical kinetic or thermodynamic control in order to analyze, predict, and understand the full diversity of chemical reactivity. Our work highlights the possibility of reactions 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.

Probing the Reaction Dynamics of Hydrogen-Deficient Hydrocarbon Molecules and Radical Intermediates via Crossed Molecular Beams

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The objectives of this project are to understand the formation and growth mechanisms of important polycyclic aromatic hydrocarbons (PAHs) and their hydrogen-deficient precursor molecules from the ‘bottom up’ in combustion processes of hydrocarbon-based fuel. This presents a major unsolved problem in combustion chemistry. 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) under single collision conditions: the propargyl (C_3H_3; X2B1) and the phenyl radical (C_6H_5; X2A1), respectively. Our studies focus on three key systems:

First, we explore the hitherto poorly understood stability (unimolecular decomposition) of one of the key RSFRs: the propargyl radical (C_3H_3; X2B1). This is achieved by accessing various regions of the C_3H_3 surface through the bimolecular radical–neutral reaction of methylidyne (CH) with acetylene (C_2H_2;

X1Sg+) and the atom–radical reaction of ground state carbon atoms (C(3Pj)) with vinyl radicals (C_2H_3; X2A') over a wide range of collision energies from 10 to 30 kJmol-1.

Second, we aim to elucidate the collision energy-dependent dynamics of the reaction of the resonantly stabilized propargyl radical with another propargyl radical leading via chemically activated C_6H_6 intermediates to C_6H_5 isomers like the phenyl radical and/or acyclic isomers. So far, this reaction has never been studied under true single collision conditions, and the detection of the phenyl radical as an aromatic ring product of the propargyl radical self reaction under collision-less conditions has remained elusive so far.

Third, we investigate the chemical dynamics of the phenyl radical (C_6H_5; X2A1) under single collision conditions with selected hydrocarbons to form individual PAHs with indene and naphthalene cores and their acyclic isomers. This shall be achieved by reacting phenyl radicals with allene (H_2CCCH_2), methylacetylene (CH_3CCH), propylene ($CH_3C_2H_3$), diacetylene (HCCCCH), vinylacetylene ($HCCC2H_3$), and 1,3-butadiene ($C_2H_3C2H_3$) and its isomers in crossed beam studies at low collision energies. These studies access the important C9Hx (x=8,10) and C10Hx (x=6,8,10) PESs, among them crucial combustion intermediates with indene and naphthalene cores. As of to date, no experiment has been conducted in which an individual PAH (like) species is formed via a bimolecular gas phase reaction under single collision conditions in crossed beams experiments.

To achieve these goals, we conduct state-of-the-art crossed molecular beam experiments over a wide range of collision energies from 10 to 180 kJmol-1 in a hydrocarbon-free, crossed molecular beam machine at The University of Hawaii. The following detection schemes are employed: (1) tunable soft electron impact ionization (8-30 eV) and hard electron impact ionization (80 eV) of the neutral products followed by an angular-resolved detection of the ions via time-of-flight mass spectrometry and—for selected systems like naphthalene—laser induced fluorescence and (2) supersonic beams of the open-shell reactants are generated via laser ablation (P), photolysis (P), and flash pyrolysis (P, C) (P = pulsed beams, C = continuous beams). The results of the scattering experiments are combined with ab initio (Alexander Mebel) and quantum scattering calculations (Martin Head-Gordon) as well as 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 (polycyclic aromatic) hydrocarbon molecules and their radical precursors. This also assists to comment on the vital role of these processes to form distinct isomers in combustion flames. These data are very much required by the combustion chemistry community to understand the formation of carbonaceous nanostructures as well as of polycyclic aromatic hydrocarbons (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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Funding: $112,000

The density-functional approximations, long a workhorse of computational solid-state physics, have fundamental limitations in their ability to predict bulk properties of importance such as band gaps, ionization energies, and excitation energies. Researchers in both quantum chemistry and solid-state physics communities are beginning to overcome this problem by applying systematic and thus predictive electron-correlation methods based on perturbation (MP), coupled-cluster (CC), and Green's-function (GF) theories to polymers and solids, potentially transforming the computational aspect of the field. The demonstrated high accuracy of these methods for the electronic part of the energies furthermore ushers a new field of quantitative theories for anharmonic lattice vibrations in solids. These will not only increase the accuracy of calculated phonon energies, but they can also account for resonances and vibrational effects on lattice structures. Capitalizing on our extensive development efforts on systematic electron-correlation and anharmonic vibrational theories for molecules that have been continuously supported by DOE, we propose generalizing these methods to infinite periodic systems in one, two, and three dimensions in this renewal proposal.

For electrons, we will explore new mathematical schemes that will dramatically speedup these electron-correlation calculations, which are otherwise too expensive for solids. They involve various approximations in the dimension unique to solid-state calculations: the reciprocal (k) space. We will develop (1) the logarithm MP, CC, and GF methods, in which exponential downsampling in the k space in the Brillouin-zone integrations is applied, (2) the hybrid CC/MP method, which uses CC for bands near Fermi levels and MP for others, (3) the size-extensive configuration interaction (CI) method for metals, which introduces certain k-dependent restrictions of excitation amplitudes to ensure its size extensivity and efficiency, and its application to the metallic (equidistant) phase of polyacetylene, and (4) the explicitly correlated GF for the quasi-particle energies of extended systems. Furthermore, we approach solids' electronic structure with a localized-orbital scheme, applying MP and CC methods to hydrogen-bonded crystals. With this, we aim at resolving controversies surrounding the interpretation of inelastic neutron scattering from ice and reproducing quantitatively the pressure dependence of Raman scattering from solid hydrogen fluoride.

For vibrations, we will establish a whole new array of vibrational theories for anharmonic lattice vibrations (phonons); we will generalize the vibrational self-consistent field (VSCF), vibrational MP (VMP), and vibrational CC (VCC) to solids under periodic boundary conditions and analyze the size dependence of their formalisms. We will implement these methods with due attention to the issues of computational cost (efficiency), potential energy surface representations, size extensivity, and orbital invariance. We will apply these methods to (1) phonon dispersion curves of polyacetylene and (2) the pressure dependence of solid hydrogen fluoride, both of which are coupled electron-correlation and anharmonicity problems. We will be developing electronic and vibrational theories for solids in concert to obtain unique quantitative insights which cannot be obtained with either alone. We also plan constructing user-friendly and robust computer software that implements these new methods.

Theoretical Studies of the Reactions, and the Spectroscopy of Radical Species Relevant to Combustion Reactions and Diagnostics

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PHOTOELECTRON SPECTROSCOPY OF RADICAL SPECIES

(A) $CH_2(OH)O^-$. We are continuing our work on the photoelectron spectra of derivatives of the methoxide anion, CH_3O^-, which reveal the vibronic spectra of the corresponding neutral radicals. The spectra reflect the interstate coupling due to accidental conical intersections descendent from the 2E state symmetry-required conical intersections in methoxy. Previously we have reported results for isopropoxy and ethoxy which complement work by the groups of Neumark (UC Berkeley), Miller (Ohio State University) and Lineberger (University of Colorado). We are presently finishing up a study of the hydroxy methoxide anion, CH_2 $(OH)O^-$, which is derived from methoxide by an $H \rightarrow OH$ substitution. We will report a description of the two state quasi diabatic Hamiltonian we have developed to represent accurate ab initio potential energy surfaces coupled by an accidental seam of conical intersections. This task was complicated by large amplitude motion of the OH group which required use of our recently developed quartic vibronic coupling model. We will also report the simulated photoelectron spectra derived from this Hamiltonian.

(B) With the advent of new high resolution photoelectron detection techniques including the slow electron velocity-map imagining (SEVI) method, it is now possible to detect, weak spectral lines, with low excitation energies, attributable to energetically remote conical intersections. Our simulations, whose increased accuracy is due to the introduction of diabatic representations based on the higher order polynomials noted above, will assist in identifying these spectral features, in radicals relevant to combustion.

NONADIABATIC REACTION DYNAMICS

(A) $OH(A)+H_2 \rightarrow H_2O + H$ or $OH(X) + H_2$. We are in the process of determining a coupled quasi-diabatic state Hamiltonian for the description of the quantum dynamics of the captioned reaction, an archetypical electronically nonadiabatic quenching process, studied experimentally by several groups including those of Lester (University of Pennsylvania) and Davis (Cornell). We have determined a suitable multireference configuration interaction expansion and are currently determining the relevant extrema, minima, transition states and seams of conical intersection. The quasi-diabatic Hamiltonian required for this project differs qualitatively from that required to describe $CH_2(OH)O$. In the $CH_2(OH)O$ study a nonredundant set of point group symmetry-adapted internal coordinates were used to construct the quasi-diabatic Hamiltonian. Here the existence of dissociative channels requires functions capable of describing bond breaking (we use an overcomplete set) and the use of the complete nuclear permutation-inversion group rather than point group symmetry.

(B) $OH(A)+CO \rightarrow CO_2 + H(2S)$, $O(3P)+HCO(X)$ or $OH(X)+CO$. (In collaboration with Dr. Marsha Lester's group at University of Pennsylvania.) The captioned nonadiabatic quenching reaction is being studied experimentally in Dr. Marsha Lester's group. In support of these experiments, Julia Lehman, a student in

Dr. Lester's group, is carrying out nonadiabatic electronic structure calculations in collaboration with students in my group. By identifying nonadiabatic pathways attributable to conical intersections, these calculations are expected to provide valuable insights into the more diverse, when compared to $OH+H_2$, mechanistic pathways available in this reaction.

Dynamics of Activated Molecules

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The focus of my DOE-funded research program is to investigate collisional energy transfer of molecules with large amounts of internal energy under conditions that are relevant to combustion environments. Collisional energy transfer is ubiquitous in gas-phase chemistry and often controls overall reaction rates and branching ratios. We use high resolution transient IR absorption to characterize the energy transfer pathways that are responsible for the collisional cooling of high energy molecules. We measure the full distribution of exchanged energy and characterize the energy partitioning in the collision products. Determination of energy transfer rate constants yields a direct comparison with collision models that use, for example, Lennard-Jones potentials. Our current project is to investigate collisions between highly vibrationally excited pyrazine (E=37900 cm-1) with HCl.

In the past year, we have put major effort into developing the instrumentation to use a high power mid-IR optical parametric oscillator (OPO) as an IR probe source for studying collisional energy transfer of highly excited molecules. Previously we used a combination of mid-IR diode lasers and an F-center laser for transient IR probing of scattered molecules that have absorption in the region of 2.5-4.5 microns. However, we ran into serious trouble some time ago when our F-center laser suffered irreparable damage, leaving us without an IR source to probe molecules that absorb between 2.5 and 3.3 microns. For HCl probing, the IR absorption at 3.3 microns lies just to the short wavelength side of the effective lasing region for lead salt diodes, and our efforts to measure collisional energy transfer of HCl were plagued by low signal to noise ratios and irreproducible results due to large laser instability. The new OPO system solves these problems by providing an intense and tunable source of IR light in the region 2.5-3.9 microns. We have fully incorporated the OPO into one of our transient absorption spectrometers and are using this instrument to measure collisional energy gain in HCl. We have achieved a 250-fold improvement in our signal to noise ratio for HCl transient measurements. We are currently characterizing the nascent full distribution of states and their velocity distributions.

Investigation of Non-Adiabatic Effects in Reactive and Inelastic Collisions of Molecular Combustion Intermediates

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Funding:	$152,000

Nonadiabatic dynamics also plays a key role in reactions of the radical species which occur in key combustion reaction pathways and which are used as optical probes of combustion systems. Alexander will extend the methodologies he has developed for the quantum description of reactive and inelastic collisions on multiple PES's. He will then apply these methods to the study of several exemplary radicals of importance in combustion environments, namely OH, CH_2, SH and SO. A special focus will be barrierless insertion reactions, which typically have large cross sections at low collision energy, and so become very important near thresholds.

The summary goals of the present proposal are the following:

(1) Continue the development of a rigorous framework for the fully-quantum description of elementary reactions when both reactant and product channels involve open-shell species, so that the reaction will involve multiple potential energy surfaces.

(2) Use this exact framework to develop approximation methods capable of including correctly the spin- and electronic-orbital character of the states of reactants and products while still retaining a single-potential-energy-surface description of the dynamics.

(3) Extend previous work on inelastic electronic-state-changing collisions from diatomic to triatomic targets.

(4) Continue the development of sophisticated, publicly-distributed software packages for the quantum treatment of inelastic and reactive dynamics of small molecules, in which multiple potential-energy-surfaces and multiplet state structure must be included.

(5) Use these new methods and software to carry out a number of detailed landmark studies of collision dynamics of several radicals of particular importance in combustion environments. The results of these careful investigations will be critically important in assessing the accuracy both of more approximate methods as well as new experimental techniques which can then be extended to larger systems.

Computer-Aided Construction of Chemical Kinetic Models

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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. Because these large models contain so many numerical parameters (e.g., rate coefficients, thermochemistry) one never has sufficient data to uniquely determine them all experimentally. Instead one must work in “predictive” mode, using theoretical values for many of the numbers in the model and, as appropriate, refining the most sensitive numbers through experiments. Predictive chemical kinetics is exactly what is needed for computer-aided design of combustion systems based on proposed alternative fuels, particularly for early assessment of the value and viability of proposed new fuels. Our research effort is aimed at making accurate predictive chemical kinetics practical; this is a challenging goal which necessarily includes a range of science advances. Our research spans a wide range from quantum chemical calculations on individual molecules and elementary-step reactions through the development of improved rate/thermo estimation procedures, the creation of algorithms and software for constructing and solving the simulations, and the invention of methods for model-reduction, while maintaining error control through comparisons with experiment. Many of the parameters in the models are derived from quantum chemistry, and the models are compared with experimental data measured in our lab or in collaboration with others.

In February 2011, we released Reaction Mechanism Generator (RMG) version 3.3, which builds a reaction mechanism valid at a set of user-specified conditions (initial composition, pressure, temperature, timescale), and automatically identifies and computes the chemically-activated reactions and their pressure-dependent rate coefficients. In a paper accepted for publication in PCCP we compared three different methods for computing these k(T,P). The new software also works for liquid-phase reactions (e.g., in fuel droplets), using a variety of methods to estimate the largest solvent effects on thermochemistry and rate coefficients. This is the first automated mechanism generation program suitable for liquid phase reactions. The new version of the RMG software automatically spawns quantum chemistry jobs to compute the thermochemistry of fused cyclic species, since this thermochemistry is not estimated accurately by group additivity approaches. During 2011 researchers from several universities and one company came to be trained in the use of this software.

The large kinetic models are difficult to use in CFD codes, so we continue to develop model-reduction and advanced numerical methods to make solving them more practical. We are about to submit a paper clarifying the mathematical relationships between model-reduction methods, and along with Gil Strang, we are about to submit a new operator-splitting method which is superior to the conventional Strang splitting.

We continue to use quantum chemistry to improve the rate coefficients in the models. In collaboration with Alexander Mebel, we computed the rates for C_6H_5 + C_3H_6. Some of this forms allyl directly, but much of it reacts via an adduct. We have computed the subsequent chemically-activated isomerizations and dissociations, and compared them with Ralf Kaiser's experimental data in a recently-submitted jointly authored manuscript.

Spectroscopic and Dynamical Studies of Highly Energized Small Polyatomic Molecules

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The goal of this project is to develop the experimental techniques, population diagnostics, interpretive concepts, and spectroscopic pattern-recognition schemes needed to reveal the large-amplitude motions that 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, particularly the HNC - HCN and HCCH - CCH_2 isomerization systems.

A complex chemical mechanism proceeds by a sequence of elementary steps, each of which can be studied in detail by state-of-the-art experimental Physical Chemistry techniques. Unimolecular decomposition reactions have played a central role in the development of key concepts and experimental techniques in Physical Chemistry. Unimolecular reactions are not only among the elementary steps of complex chemical mechanisms, but they are often encountered as independent entities in combustion and photochemical processes. Moreover, the state- and species-specific study of unimolecular reactions provides key insights into the non-equilibrium behavior of highly excited molecular systems. The potential energy surfaces and the concomitant dynamics of highly energized, medium-sized molecular systems are now within the reach of high-level calculations; however, experimental observations (some of which employ experimental techniques developed in our laboratory) remain the only way to test theoretical predictions.

The relevance of this project to combustion chemistry is the development of new experimental methods (such as Stimulated Emission Pumping and Chirped Pulse millimeter-Wave spectroscopy) to obtain information about those rare eigenstates that encode large amplitude motion and thereby map the those chemically most interesting regions of a potential energy surface that are proximal to the minimum energy isomerization path.

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

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This research program focuses on the development and applications of new generations of ab initio electronic structure methods and computer codes, exploiting the exponential coupled-cluster (CC) wave function ansatz, which can provide an accurate description of chemical reaction pathways, radicals, biradicals, potential energy surfaces (PESs), properties other than energy, and electronic excitations in molecular species. The goal is to design and apply affordable computational methods that enable precise modeling of molecular processes and properties relevant to combustion, catalysis, photochemistry, and photobiology. Among the most promising methods developed in this program are (1) the renormalized CC and equation-of-motion CC (EOMCC) approaches, and the low-order scaling, local correlation extensions of the conventional and renormalized CC methods to larger molecular systems involving hundreds of correlated electrons; (2) the active-space CC and EOMCC methods; and (3) the genuine multi-reference CC (MRCC) theories. The main focus is on methods that can balance high accuracy with the relative ease of use and relatively low computer costs compared to other quantum-chemistry approaches that aim at similar accuracies. This being, so that one can study chemical processes and phenomena involving complex molecular problems with dozens or hundreds of non-hydrogen atoms, in addition to the more traditional smaller systems. The renormalized CC methods and their open-shell, local correlation, and excited-state generalizations extend the standard 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 that can be performed by non-experts. The active-space CC and EOMCC approaches, and their open-shell generalizations via the electron attached (EA) and ionized (IP) theories as well as the genuine MRCC methods have the flexibility that enables accurate ab initio calculations for all kinds of closed- and open-shell electronic states, with manageable computer costs, including systems characterized by strong electronic near-degeneracies that cannot be handled by single-reference approaches.

Methods pursued in this program can effectively utilize modern multi-node computer architectures and are well suited for pursuing novel coding strategies, such as the automated and parallel computer implementations. They address two main challenges of electronic structure theory: (1) the development of practical and systematically improvable computational schemes that can provide a balanced and accurate description of closed- and open-shell systems, and the rapidly changing electron correlation effects along reaction coordinates and in electronic excitations, and (2) the development of algorithms that can reduce prohibitive costs of traditional high-accuracy ab initio calculations by orders of magnitude by directly attacking the scaling laws that define the dependence of computer costs on the system size. Methods developed in this program are shared with the community by incorporating them in the GAMESS package.

Developing a Predictive Model for the Chemical Composition of Soot Nanoparticles: Integrating Model and Experiment

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The dimerization of polycyclic aromatic hydrocarbons has been regarded as one of the most important processes in soot formation. In particular, the dimerization of pyrene is widely used as a nucleation process in many soot modeling studies. In this work, we report on a theoretical study using molecular dynamics simulations to investigate the role of various polycyclic aromatic hydrocarbon molecules, including pyrene, in the soot formation process. Our simulation results indicate that the collision efficiency is primarily influenced by two major factors, temperature and molecular mass, and the pyrene dimerization route is more dependent on the flame temperature conditions than those of larger polycyclic aromatic hydrocarbons. There are also other important factors that influence collision efficiency, such as molecular curvature, that can induce complex behaviors in various temperature conditions. The results from this study can be utilized to obtain accurate nucleation rates for soot models.

The Effects of Oxygenated Fuel Compound Structure on Combustion and Pollutant Reaction Chemistry

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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 a 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 ester compounds through comprehensive experimental and modeling efforts. The effects of varying carbon content and chemical structure of representative esters are examined through ignition studies. Ignition delay time measurements are used to quantify the effects of chemical structure on reaction rates. Gas chromatography of stable intermediate species is used to interrogate the effects on decomposition and oxidation pathways and on formation of sentinel species for particulate production (e.g., propene). Fundamental studies of strong and weak ignition phenomena are used to develop improved methods to quantitatively validate reaction kinetics at moderate temperatures and high pressures. The outcomes of this work provide quantitative assessment of the reaction pathways important in fuel compounds as a function of the critical chemical properties of the compounds and at conditions directly relevant to modern combustion systems.

Variational Transition State Theory

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This project involves the development of variational transition state theory (VTST) including optimized multidimensional tunneling 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 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, and methods to interface reaction-path and reaction-swath dynamics calculations with electronic structure theory. 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.

Hydrocarbon Radical Thermochemistry: Gas-Phase Ion Chemistry Studies

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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. Existing guided ion beam tandem mass spectrometry experiments are being complemented by development of a Quadrupole Ion Trap/Time-of-Flight tandem mass spectrometer.

Quantum Dynamics of Elementary Chemical Reactions

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We have been working on a new potential energy surface for the HOCO system, on which the second most important combustion ($HO + CO \rightarrow H + CO_2$) takes place. This is a difficult system because of the open-shell nature of the HOCO radical. Existing potential energy surfaces have been shown to give incorrect dynamics results when compared with experiment, and an accurate potential energy surface is urgently needed. We have used the CCSD(T) approach to map out various key areas of the potential energy surface. Once it is developed, we plan to carry out both classical and quantum dynamical studies of the reaction dynamics on this new and more accurate potential energy surface.

We are also working on the N + H_2 reaction, taking into consideration of the spin-orbit coupling between the doublet and quartet surfaces developed by Richard Dawes. We aimed at addressing the quantum dynamics of this reaction which proceeds via an insertion pathway on the doublet state and abstraction on the quartet state. The non-adiabatic coupling between the two allows the system to access two different reaction pathways. Comparison with the recent experimental data from Tim Minton's group will help to understand the reaction dynamics of this prototypical reaction.

Another system we are working on is the photodissociation of ammonia, which is known to have many intriguing features such as tunneling and non-adiabatic couplings. We are collaborating with David Yarkony on the full-dimensional quantum dynamical model based on highly accurate potential energy surfaces fit by the Yarkony group. The dynamics is expected to yield insights into the multi-dimensional dissociation dynamics of this interesting system.

Dynamics of Radical Reactions in Biodiesel Combustion

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The proposed research will use computational chemistry to investigate the dynamics of unimolecular reactions of peroxy radicals (ROO•) important in the combustion of biodiesel fuel. The reactions of greatest interest are the 1, 2 elimination of HO_2 and transfers of hydrogen atoms from a carbon atom to the peroxy radical center (1,n H-shift reaction). A series of modest-sized model compounds will serve as excellent mimics of biodiesel fuel (fatty acid methyl esters) while enabling reliable and accurate computations. Quantum chemistry will be used to study the effects of molecular structure on the heights of reaction barriers in the model peroxy radicals. Variational transition state theory will be used to calculate the semi-classical rate constants for the reactions of interest. Multidimensional tunneling calculations will be carried out to determine how quantum mechanical effects change the rate constant, especially for the H-shift reactions. RRKM/Master Equation calculations will be used to determine the extent of chemically activated reactions on the complicated potential energy surface, compute product yields for comparison with experiment, and determine phenomenological rate constants.

The combustion chemistry of peroxy radicals presents an on-going challenge for experiments; peroxy radicals are not readily detected by mass spectrometry and are hard to distinguish spectroscopically in a combustion environment. The key intermediates in diesel ignition are hydroperoxy-substituted alkyl radicals (e.g., $\bullet CH_2CH_2OOH$) produced from peroxy radical 1,n H-shift reactions, but these crucial intermediates have been impossible to detect experimentally. While extensive experimental efforts have yielded significant insights into the chemistry of alkane-derived peroxy radicals, peroxy radicals with the ester and olefin functional groups relevant to biodiesel fuel have scarcely been studied. The computational research proposed here is necessary for understanding the combustion of biodiesel fuels.

Quantum calculations, taking advantage of recent developments in density functionals and composite electronic structure approaches, will provide insights into the effects of molecular structure on barrier heights, leading to structure-reactivity relations. Variational transition state theory will enable determination of dynamical effects, such as how the position of the transition state varies from that of the saddle point. Tunneling calculations will enable comparison with experiments, including those using deuterated compounds, and reveal how molecular structure and ring-size in cyclic transition states changes the extent of small-curvature versus large curvature tunneling.

The results of the proposed research will provide new insights into the fundamentals of combustion chemistry, particularly for biodiesel fuels, for which molecular-level data is sparse. This research sets the stage for accurate and reliable kinetic modeling of combustion of biodiesel fuel, which will lead to improved efficiency of biodiesel combustion and less pollution. To the extent this research supports increased use of biofuels, this work would increase our country's energy independence, reduce emissions of hazardous air pollutants, and recycle CO_2, a major greenhouse gas.

Threshold Photoelectron Photoion Coincidence (TPEPICO) Studies: The Road to +/-0.1 kJ/mol Thermochemistry

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The threshold photoelectron photoion coincidence (TPEPICO) technique is utilized to investigate the dissociation dynamics and thermochemistry of energy selected medium to large organic molecular ions. The reactions include parallel and consecutive steps that are modeled with the statistical theory in order to extract dissociation onsets for multiple dissociation paths. These studies are carried out with the aid of molecular orbital calculations of both ions and the transition states connecting the ion structure to their products. The results of these investigations yield accurate heats of formation of ions, free radicals, and stable molecules. In addition, they provide information about the potential energy surface that governs the dissociation process. Isomerization reactions prior to dissociation are readily inferred from the TPEPICO data.

Kinetics and Product Channel Studies in Combustion Chemistry

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This proposal describes experiments designed to improve our understanding of the detailed kinetics involved in combustion chemistry. Emphasis is placed on reactions of small nitrogen-containing radicals and molecules that play a crucial role in the formation and removal of NOx pollutants. Time-resolved infrared diode laser spectroscopy and laser-induced fluorescence spectroscopy will be used to probe reactants and products in reactions such as NCCO + NOx, HCCN + NOx, HCC + NOx, CN + R-OH, etc.

These reactions may exhibit complex chemistry involving numerous product channels. Major goals of this project include the quantitative measurement of product branching ratios as well as total rate constants of these reactions. Such data will provide crucial information required for effective modeling of complex combustion systems.

Spectroscopic Detention, Characterization and Dynamics of Free Radicals Relevant to Combustion Processes

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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.

Dynamical Analysis of Highly Excited Spectra

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The highly excited vibration-rotation dynamics of small molecular species, including those approaching the threshold of reaction, are crucial to understanding fundamental processes important for combustion. 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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Hydroxyl radicals are important in combustion and atmospheric environments, where they are often detected by laser-induced fluorescence (LIF) on the A-X band system. However, collision partners known to quench electronically excited OH radicals are ubiquitous in these environments. Thus, great effort has been made to quantify the rates and/or cross sections for collisional quenching, so that its effects on LIF signals may be taken into account to allow an accurate determination of OH concentrations. Despite extensive kinetic measurements, 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 electronically excited OH radicals by molecular partners (M = H_2, O_2, N_2, CO, CO_2, H_2O) of significance in combustion environments.

Current research focuses on the outcomes of collisional quenching of electronically excited OH radicals. Specifically, the experimental studies examine reactive quenching processes that generate chemically distinct products as well as nonreactive quenching processes that return OH to its ground electronic state, the latter with an emphasis on the energy transferred to the collision partner. The observed product state distributions from reactive and nonreactive quenching processes will be used to identify the forces acting on the nuclei as the system switches from the electronically excited to ground state potential energy surface. The systems investigated and experimental methods utilized will be expanded to probe previously unobserved outcomes of collisional quenching. Finally, collaborations will be developed with theoretical groups to obtain a comprehensive model for quenching consistent with kinetic rate measurements, product branching ratios, quantum state distributions, and kinetic energy release.

Advanced Nonlinear Optical Methods for Quantitative Measurements in Flames

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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.

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 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. This laser system has a pulse length of 60 fs and an average power of over 10 W at the fundamental wavelength of 800 nm. The fundamental beam was used as the Stokes beam, as the chirped probe beam, and to pump an OPA to obtain the 675-nm pump beam needed for N2 CARS. The greatly increased pulse energy of the 800-nm chirped-pulse-probe beam, as compared to the previous configuration with a 675-nm probe beam, results in a significant increase in the signal-to-noise ratio of the single-pulse measurements. We have begun to explore methods for quantitative single-pulse concentration measurements and the use of polarization suppression of the nonresonant background in single-pulse temperature measurements. The time-dependent density matrix methods that we have developed as a result of ongoing support from this program are ideally suited for the simulation of the interaction of fs laser radiation with molecular resonances.

Experimental Characterization of the Potential Energy Surfaces for Conformational and Structural Isomerization in Aromatic Fuels

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Under fuel-rich conditions, reactions that lead toward soot formation occur, with aromatic molecules and resonance-stabilized radicals playing key roles as intermediates. A key objective of this research program is 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 the goal of providing deeper insight to the chemistry involved in the combustion and pyrolysis of wood and biofuels. Finally, we continue to study molecules in which two or more electronic states are in close proximity, and are coupled by vibrational motion involving low frequency torsions.

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

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We seek to utilize theoretical methods to understand the gas phase structures and energies of the combustion and pyrolysis reactions of the molecular constituents of asphaltenes contained in oil sand and oil shale. Asphaltenes represent an untapped source of hydrocarbon fuels 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 molecules that contain 4-10 fused ring cores, with alkyl chain arms extending from the core. Sulfur and nitrogen may also be present. Very little is known about the reaction pathways of these heteroaromatic species. We propose to theoretically characterize the combustion and pyrolysis reaction channels available to asphaltene constituents, such as methyl thiophene and 2-methylbenzo-thiophene. Once we have established the proper procedures for characterizing these smaller model systems, we intend to characterize larger fused polyaromatic systems found in asphaltenes, such as octylphenanthrene and tetracene.

Modeling combustion reactions, particularly among larger heteroaromatic systems, mandates an accurate and efficient characterization of radical intermediates. This is a rapidly growing field, and we plan to implement four of the most recently developed methods for the proper characterization of radicals; two such methods (Spin Flip and Completely Renormalized Coupled Cluster) have been previously developed with DOE-BES support. These are ambitious projects; but, as multicore processors become faster and more affordable, and as significant methodological advancements are made, it becomes possible and practical to accurately characterize larger systems.

This project will require a significant investment of computational resources. National grids will be utilized. In addition, local computing resources are necessary for student training and testing. These local resources will be provided by the University of Richmond. This project is expected to evolve beyond the initial 3-year funding cycle to include the development of kinetic models for combustion of asphaltene components using Variational Transition State or Rice-Ramsperger-Kassel-Marcus theories.

Detailed Studies of Hydrocarbon Radicals: C2H Dissociation Dynamics

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Studies are underway of C_2H excited state properties and dynamics from dissociation threshold to as far above D_0 as possible. The central role played by this species in hydrocarbon chemistry cannot be overstated. It is also an excellent prototype for examining important properties and phenomena: electronic states; curve crossings and associated nonadiabatic transitions; intramolecular and dissociation dynamics; and so on. It is small enough to provide experimental parent and product state resolution, and it is tractable at a high level of theory — both electronic structure and quantum mechanical nuclear dynamics, including nonadiabatic couplings. It is an example of a system in which more than two conical intersections need to be taken into account simultaneously. Complex issues range from couplings among its many electronic states to its not-yet-assigned UV spectrum. Moreover, it dissociates to C_2 + H which is certain to require care in theoretical descriptions because of the large number of C_2 electronic states. Research consists of complementary experimental studies, and theoretical calculations in support of the experimental effort. The UV absorption spectrum of expansion-cooled C_2H will be obtained via the yield spectrum for the dissociative channel: $C_2H + h\nu$ –> C_2 + H. This will be achieved by monitoring C_2 using soft ionization (i.e., electron energies of 15-16 eV are incapable of producing C_2^+ from C_2H or its precursor) while varying hν. Because of the large geometry change in going from the ground state to the B state (the CC bond length increases by 0.21 Å and the CCH angle goes from 180° to 116°), and because only low $3(^2A')$ vibrational levels fluoresce, the dissociative channel dominates the UV spectrum.

Photoinitiated Reactions of Radicals and Diradicals in Molecular Beams

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Radicals and diradicals are essential intermediates in combustion and environmental chemistry. Our long-term program is focused on studies of the photoinitiated decomposition of hydroxyalkyl radicals and carbenes in the gas phase using state-resolved probes. These studies offer opportunities to address fundamental issues related to the open shell nature of these species and the multitude of nonadiabatic interactions that are involved in their evolution to products. The chosen radicals are amenable to treatment by high-level theory. Hydroxyalkyl radicals are important intermediates in combustion reactions such as the reaction of OH with olefins but compared to their isomers, the alkoxy radicals, relatively little is known about their spectroscopy and decomposition on the ground and excited states. Diradicals are important in synthetic chemistry and photochemistry, and play a role in atmospheric, combustion and interstellar chemistry.

Time-sliced velocity map imaging, which allows determination of kinetic energy distributions with high resolution and sensitivity, will be used to monitor hydrogen fragments, making it possible to derive the internal energy distributions in the co-fragments with vibrational resolution. The specific projects are:

(1) The unimolecular reaction of CH_2OH and its partially deuterated isotopologs on the ground state initiated by overtone OH excitation to above the barriers to CH_2O + H dissociation and $CH_2OH \leftrightarrow CH_3O$ isomerization. The unique aspect of this study is the direct pumping of the dissociation coordinate—the OH stretch. The internal state distributions in the products will be determined by slice imaging.

(2) The photodissociation dynamics of hydroxymethyl and hydroxyethyl radicals via multiple conical intersections between Rydberg and ground states. Emphasis will be placed on internal state distributions in the aldehydes and hydroxycarbene products generated by O-H and C-H bond fission, respectively, and comparisons made with theory. This study will be the first to probe the internal state distribution in HCOH, the isomer of formaldehyde.

(3) This project will examine the excited state spectroscopy of triplet methylene and the dynamics of conical intersections between Rydberg and valence states that lead to H + CH and H_2 +C products. These will be compared with available high-level electronic structure and dynamical calculations. Singlet hydroxycarbene (HCOH) will be studied with initial emphasis on production and diagnostics.

The experimental approaches are (1) the preparation of molecular beams of radicals by pyrolysis, photolysis, and chemical reactions; (2) the diagnostics of reactants and products by resonance enhanced multiphoton ionization (REMPI) and translational and photofragment yield spectroscopy; (3) the implementation of laser excitation schemes that include overtone pumping and UV and IR+UV excitation to reach dissociative states; and (4) the study of dissociation dynamics by time-sliced velocity map imaging of photofragments. Theoretical collaborations with the groups of Anna Krylov, Joel Bowman, David Yarkony, Larry Harding and Stephen Klippenstein are envisioned.

Theoretical Modeling of Spin-Forbidden Channels in Combustion Reactions

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

This scope of our research program is on theoretical studies of spin-forbidden channels in combustion reactions and reaction intermediates. It combines method developments necessary for characterizing the electronic part of transitions between different electronic states and applications to prototypical reactions relevant to combustion. It also includes tools to facilitate interpretation of experimental results. In particular, we are motivated by photoionization and photodetachment experiments that are broadly used in the combustion community. For example, photoionization is used as a tool to identify transient reaction intermediates in combustion processes. Photodetachment can be employed to create radicals implicated in combustion mechanisms in order to study their properties and spectroscopic signatures.

The methodological part consists of (1) development of complex-scaled equation-of-motion coupled-cluster (cs-EOM-CC) methods for modeling autoionizing (resonance) states as well as photoionization and photodetachment cross sections, (2) implementation and benchmarking of non-collinear spin-flip DFT, and (3) improvements of the charge-stabilized DIP (double ionization potential) approach.

cs-EOM-CC allows one to model electronically excited states embedded in the ionization continuum, which are accessed in high-energy ionization processes. Moreover, via Green's function formalism, the L2 integrable solutions of cs-EOM-CC eigen-problem can be used to evaluate photoionization cross sections. Both resonance states and photoionization cross sections are important for quantitative modeling of photoionization efficiency curves, and these computational tools may aid the interpretation of synchrotron radiation experiments used to identify transient combustion intermediates.

SF-DFT is an inexpensive yet efficient method for modeling bond-breaking and diradicals. Our original (collinear) implementation has been extended by other groups to pure functionals via non-collinear formalism, which resulted in improved accuracy and reliability. We are implementing and benchmarking non-collinear DFT, and will extend it to long-range corrected functionals. Target applications include large hydrocarbon diradicals implicated in combustion processes.

EOM-DIP is the method of choice for oxygen-containing diradicals, however, its applications have been limited by the instabilities of dianion references. We developed a solution based on the charge-stabilization approach. We are implementing a non-iterative energy correction accounting for the interaction of the target states with the stabilizing potential to further improve the accuracy of charge-stabilized DIP.

Our computational studies include application of new methodology to combustion intermediates; for example, the characterization of vibrational states and dynamics of the CH_2OH radical.

Kinetics and Spectroscopy of Combustion Gases at High Temperatures

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Funding:	$160,000

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 and (2) shock tube studies of reaction kinetics relevant to combustion.

Species currently being investigated in the spectroscopic portion of the research include C_2H_4 (at 10.5 microns), H_2O (at 2.5 microns), and CO_2 (at 2.7 microns). New efforts are also being made to study formaldehyde (CH_2O) in the UV (near 325 nm) and in the IR (near 3.4 microns), and CO (near 4.6 microns).

In parallel with these spectroscopic studies, kinetics research has advanced on several fronts. (1) Our OH diagnostic has been used to measure the rate coefficients for a series of reactions of the alkenes +OH, including ethylene, propene, butane, and 1,3-butadiene, and of the alkanes+OH including n-pentane, n-heptane, n-nonane. (2) H_2O and OH diagnostics have been used to provide improved measurements of several hydroperoxyl radical rate coefficients in the $H_2/O_2/H_2O_2/HO_2$ system, including those for the reactions $OH + HO_2 = H_2O + O_2$ and $OH + H_2O_2 = H_2O + HO_2$. These results, together with our earlier measurements for $H + O_2 = OH + O$ and $H_2O_2 + M = 2OH + M$ have been combined to form an updated H_2/O_2 reaction mechanism.

Quantum Chemistry of Radicals and Reactive Intermediates

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Funding:	$179,000

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 DOE includes 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; a study of molecular ionization that includes both photoelectron spectra and what are known as photoion efficiency curves that is targeted towards helping to better understand studies carried out by collaborators at the Synchrotron facility at Lawrence Berkeley Laboratory; and a somewhat new (in implementation only) semiclassical approach for the calculation of molecular reaction rates that shows great promise.

Development of Kinetics for Soot Oxidation at High Pressures Under Fuel-Lean Conditions

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Funding: $159,000

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 mechanisms for soot oxidation. The objectives include understanding of the kinetics of soot oxidation by O_2 under high pressure which will require:

(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.

Universal and State-Resolved Imaging Probes of Chemical Reaction Dynamics

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Funding: $170,000

Owing to the huge societal investments in combustion-derived energy, development of new approaches that yield increased combustion efficiency, exploit renewable biofuels, and that minimize greenhouse gas emissions and tropospheric pollutants can deliver a payoff disproportionate to the initial investment. To achieve these advances, computer models sufficiently accurate to model practical combustion environments are necessary. The development of such a fully predictive understanding of combustion chemistry requires knowledge of the nature and identity of the elementary reaction mechanisms, the size of any activation barriers, the identity of reaction products, and the thermochemistry and energy disposal in the relevant species. Often these quantities are needed for conditions at which measurements are impossible, so an understanding of the underlying principles is an essential aspect of the successful development of accurate predictive models for real chemical systems.

This program exploits recent advances in high-resolution ion and electron imaging in imaging applications of crossed molecular beam scattering, and in development of new approaches, to extend the range of chemical dynamics studies into the frontier areas outlined above. A key aspect of this program is combining universal ion imaging probes providing a global perspective 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.

The specific objectives of our program remain: to explore the role of nonadiabatic processes and transient species in these reactions, to identify novel reaction pathways and mechanisms and to investigate their importance, to extend the range of powerful dynamics studies to more complex polyatomic systems, and to benchmark a range of theoretical methods. This research is conducted via photodissociation, photoionization and reactive scattering experiments using state-of-the-art molecular beam machines, and vacuum ultraviolet lasers in conjunction with ion imaging techniques. Our studies often involve collaboration with leading theoretical groups. An ongoing parallel effort is made to develop new tools and experimental methods with which to achieve these goals.

Dissociation Pathways and Vibrational Dynamics in Excited Molecules and Complexes

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Funding:	$175,000

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.

The experiments begin with molecules that contain some of the same features as the prototypical ammonia (NH_3) molecule along with other interesting aspects. For example, aromatic molecules have an additional electronically excited state and, in some cases, an additional conical intersection that can participate in the decomposition. Some of these molecules have multiple dissociation pathways whose relative importance depends on the initial vibrational excitation. Because the presence of an adduct can change the dissociation dynamics at a conical intersection, the second part of the proposed research investigates the vibrationally mediated photodissociation of complexes. The first targets are the complexes of ammonia, ammonia derivatives, and phenol with adducts such as CO, CO_2, C_2H_2, HCN, and H_2O. The combination of these molecules and adducts provides a large range of interaction energies and bonding motifs that can reveal the influence of both the adduct and the initial vibrational excitation. It is even possible that the combination of electronic and vibrational excitation will initiate new reactions within the complexes. These experiments can identify dissociation pathways, discover the factors that control the course of decompositions, and test theoretical models of the dissociation of energized molecules.

Support for Chemistry Symposia at the 2011 American Association for the Advancement of Science Meeting February 17-21, 2011

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Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$23,000

This proposal supported funding for Chemistry Symposia at the 2011 American Association for the Advancement of Science (AAAS) Meeting in Washington, DC, February 17-21, 2011. The 2011 AAAS Annual Meeting provided an important opportunity to play a prominent role in the global celebration of the 2011 International Year of Chemistry. The AAAS meeting provided an unusual opportunity to convey the excitement and importance of chemistry to a very broad audience and allows access to a large contingent of the scientific press.

The titles of the symposia were: (1) Powering the Planet: Generation of Clean Fuels from Sunlight and Water, (2) Biological Role and Consequences of Intrinsic Protein Disorder, (3) Chemically Speaking: How Organisms Talk to Each Other, (4) Molecular Self-Assembly and Artificial Molecular Machines, (5) Frontiers in Organic Materials for Information Processing, Energy and Sensors, and (6) Celebrating Marie Curie's 100th Anniversary of Her Nobel Prize in Chemistry.

Support for the symposia provided the opportunity to highlight the excitement of current chemical research, to educate the public about the achievements of chemistry and its contributions to the well-being of humankind.

The Principal Investigator is Professor Charles P. Casey of the University of Wisconsin-Madison, who was the 2010 Chair of the Chemistry Section of AAAS.

Computational and Experimental Study of Laminar Flames

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Sr. Investigator(s): Long, Marshall, YALE UNIVERSITY
Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $237,000

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. 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

Chemical Dynamics in the Gas Phase

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Tranter, Robert, ARGONNE NATIONAL LABORATORY
Students: 4 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $4,335,000

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.

High Pressure Combustion Chemistry: From Fundamentals to Accurate Models

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Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$560,000

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 (MET) through feedback loops at all levels of chemical complexity. We are developing and testing the methodology for propane, n-heptane, 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 interacts closely with the Princeton-led Combustion Energy Frontier Research Center (CEFRC).

Gas-Phase Molecular Dynamics

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Students:	4 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$1,600,000

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 the 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 these 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.

Chemical Dynamics Beamline Facility

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Students:	3 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$1,200,000

The primary purpose of this program is to support studies in chemical physics at the ALS by providing state-of-the-art experimental resources for visiting scientists and staff to undertake studies of fundamental chemical processes:

- To determine the microscopic details of the mechanisms and dynamics of primary dissociation processes and elementary chemical reactions.
- To explore the properties and decay dynamics of molecules in highly excited, transient, or metastable states.

- To study the structure, energetics and chemical reactivity of highly reactive polyatomic radicals, unusual transient species, droplets, aerosols, large biomolecules and clusters.
- To develop new spectroscopic and dynamical tools such as imaging detection of photoelectrons, 2 color pump-probe spectroscopies and pulsed field ionization techniques.
- To pioneer new directions and developments in photoionization and photoelectron spectroscopy for the enriched understanding of fundamental properties of ions and molecules to improve thermochemical parameters.
- To investigate macroscopic systems such as flame dynamics in order to develop more precise models for real combustion systems.
- Anticipated benefits to the program in particular are to provide a predictive understanding of combustion systems and a deepened understanding of chemical physics in general.

Combustion Chemistry

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Funding:	$260,000

Combustion processes are governed by chemical kinetics, energy transfer, transport, fluid mechanics, and their complex interactions. Understanding the fundamental chemical processes offers the possibility of optimizing combustion processes. The objective of our research is to address fundamental issues of chemical reactivity and molecular transport in combustion systems. 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. We emphasize studying chemistry at both the microscopic and macroscopic levels. To contribute to the achievement of this goal, our current activities are concerned with five tasks: (1) develop models for representing combustion chemistry at varying levels of complexity to use with models for laminar and turbulent flow fields to describe combustion processes, (2) develop tools to probe chemistry fluid interactions, (3) model and analyze combustion in multi-dimensional flow fields (4) determine new reaction pathways and their kinetics, and (5) develop building models for soot formation and destruction. A theme of our research is to bring new advances in computing to the study of important and computationally intensive combustion problems.

Gas-Phase Chemical Physics (experiment and theory)

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Students: 5 Postdoctoral Fellow(s), 6 Graduate(s), 0 Undergraduate(s)
Funding: $1,782,000

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.

Chemical Composition of Soot Nanoparticles

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Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $144,000

The goal of the Chemical Composition of Soot Nanoparticles SISGR 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:	11 Postdoctoral Fellow(s), 0 Graduate(s), 3 Undergraduate(s)
Funding:	$10,800,000

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:	$440,000

The goal of the High-Pressure Combustion Chemistry 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 MET paradigm (Integrated Modeling, Experiment, and Theory) 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

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Funding: $50,000

The current work is a computational chemistry effort which focuses on the molecular level description of the interactions of Gram-negative microbial membranes with subsurface materials. We are developing 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. The project is focused on the interaction of the outer microbial membrane, which is dominated by an exterior lipopolysaccharide (LPS) portion, of Pseudomonas aeruginosa with the mineral goethite and with solvated ions in the environment. Our effort using modern computational electronic structure methods 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. 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. We are studying the acidity of the acidic side groups in order to better understand the ability of these groups to bind metal ions. We need to understand the solvation properties of the metal ions in solution and their ability to bind not only to the sugars but to proteins and to other anions. One result from earlier molecular dynamics simulations is the exclusion of water from the inner hydrophobic part of the membrane. We are investigating the binding of the cations in media with different dielectric constants.

Computational and Experimental Investigations of the Molecular Scale Structure and Dynamics of Geologically Important Fluids and Mineral-Fluid Interface

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Funding: $79,000

The main objective of this joint research effort with 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 (ACC) formation and to investigate the structure, dynamics, and energetics of ions and ^2H_2O at clay-water interfaces using nuclear magnetic resonance (NMR) spectroscopy.

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 and is in press at the writing of this abstract. The key results include identification of a common combined C_2/C_3 reorientation mechanism for proximity-restricted H_2O (H_2O within 5 Å of a surface or ion) between -50°C and -20°C and the new general principle that as ionic radius decreases and hydration energy increases, ion motion becomes dominated by isotropic 2D or 3D diffusion at lower temperature. We were also able to acquire the first variable temperature ^{43}Ca NMR spectra of a ^{43}Ca-enriched calcium hectorite, which demonstrated that this general principle regarding ion motion applies to alkaline earth metal-smectites as well. Companion molecular dynamics simulations are being completed at Michigan State University now, and we expect to publish a joint NMR/MD paper examining Ca^{2+} and H_2O dynamics at the smectite-water interface before the end of the current project year. Our group broke new ground by performing the first successful ^{43}Ca and ^{25}Mg NMR studies of ^{43}Ca-enriched ACCs, which lead to several pivotal insights related to ACC structure and transformation that are currently being prepared for publication. Our results were disseminated through 10 talks at national and international meetings as well as a number of invited talks and seminars since the start of the current grant. We also visited with the Cygan and Greathouse groups at Sandia National Laboratory in May of 2011 to share our findings and talk about new ways to collaborate. Four manuscripts detailing our work are either in press, under review, or in the late stages of preparation at the authoring of this report, and our manuscript at the Journal of Physical Chemistry C will be featured on the cover December 1, 2011. Research results obtained during this past grant year also supported a new successful peer-reviewed science-theme proposal for high-field NMR instrument time at Pacific Northwest National Laboratory that secures access to these important resources for the remainder of the current grant and beyond.

Collaborative Research: Analysis and Interpretation of Multi-Scale Phenomena in Crustal Deformation Processes

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Funding:	$175,000

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, mismatching 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.

In most of the current models for materials with damage and disorder, the assumptions are often made that the damage is homogeneous, the density of defects or disorder is dilute, or each defect is embedded in the average or mean field of all the other defects. By contrast, the adoption of an approach based on statistical field theory is a general approach that yields a rich physical picture. Both classical and mean field models can be obtained as special cases, along with more general, near mean field models, together with significant corrections to the mean field results. Nonclassical modes of failure, such as spinodal nucleation, are seen in systems with interactions of long range, such as those present in models of defects embedded in an elastic solid.

Multiscale Framework for Predicting the Coupling Between Deformation and Fluid Diffusion in Porous Rocks

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Funding:	$125,000

A predictive multiscale framework is proposed 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 geomechancical processes. This research will focus on areas where severe deformations are observed, such as deformation bands, where classical phenomenology breaks down.

Multiscale geometric complexities and key geomechanical and hydraulic attributes of deformation bands (e.g., grain sliding and crushing, and pore collapse, causing interstitial fluid expulsion under saturated conditions) can significantly affect the constitutive response of the skeleton and the intrinsic permeability. Discrete mechanics (DEM) and the lattice Boltzmann method (LBM) will be used to probe the microstructure—under the current state—to extract the evolution of macroscopic constitutive parameters and the permeability tensor. These evolving macroscopic constitutive parameters are then directly used in continuum scale predictions using the finite element method (FEM) accounting for the coupled solid deformation and fluid diffusion.

A particularly valuable aspect of this research is the thorough quantitative verification and validation program at different scales. The multiscale homogenization framework will be validated using X-ray computed tomography and 3D digital image correlation in situ at the Advanced Photon Source in

Argonne National Laboratory. Also, the hierarchical computations at the specimen level will be validated using the aforementioned techniques in samples of sandstone undergoing deformation bands.

Anisotropy and Residual Stresses in Sedimentary Rocks: A synchrotron and Neutron Study

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Funding:	$120,000

Clay-rich sedimentary rocks display high intrinsic anisotropy which is significant for interpreting seismic prospecting and predicting directional diffusion. Yet there is very little quantitative information about preferred orientation of constituent minerals which is an intrinsic component of anisotropy. The anisotropy is due to three factors: the anisotropy of the single crystal that is extremely large for phyllosilicates, the non-random orientation distribution of clay crystallites, and presence of non-equiaxed porosity. While much is known about preferred orientation in monomineralic rocks such as limestone, marble and quartzite, polymineralic rocks remain enigmatic. By using novel techniques such as neutron scattering (at LANSCE), high energy synchrotron diffraction (at APS), synchrotron X-ray microtomography (at APS and ALS), as well as electron microscopy (TEM and SEM), it has become possible to quantify microstructural features and relate them to macroscopic properties such as acoustic velocities.

These investigations are not just of academic interest: Shales are intricately linked to hydrocarbon reservoirs and the direction-dependent microstructural properties of shales are of critical importance for hydrocarbon exploration and hydrocarbon migration (both oil and gas). This concerns not only shales as cap rocks of oil reservoirs, but hydrocarbon migration, shales as gas reservoirs, use of depleted reservoirs for CO_2 storage, and most recently, use of shales for nuclear waste storage.

Samples of particular interest and investigated in collaborative projects are Mt. Terri Opalinus shale, North Sea shales (various depths), diagenetic Qusaiba shale, Blakely shale, Muderong shale, as well as experimentally compacted shales for comparison. A new self-consistent model is being developed to determine aggregate elastic properties based on features such as composition, particle size and shape, particle orientation, and porosity structure.

Adding Reactivity to Structure---Oxygen-Isotope Exchanges at Structural Sites in Nanometer-Size Aqueous Clusters

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Funding:	$149,000

This proposal supported funding for Chemistry Symposia at the 2011 American Association for the Advancement of Science (AAAS) Meeting in Washington, DC February 17-21, 2011. The 2011 AAAS

Annual Meeting provided an important opportunity to play a prominent role in the global celebration of the 2011 International Year of Chemistry. The AAAS meeting provided an unusual opportunity to convey the excitement and importance of chemistry to a very broad audience and allows access to a large contingent of the scientific press.

The titles of the symposia were: (1) Powering the Planet: Generation of Clean Fuels from Sunlight and Water, (2) Biological Role and Consequences of Intrinsic Protein Disorder, (3) Chemically Speaking: How Organisms Talk to Each Other, (4) Molecular Self-Assembly and Artificial Molecular Machines, (5) Frontiers in Organic Materials for Information Processing, Energy and Sensors, and (6) Celebrating Marie Curie's 100th Anniversary of Her Nobel Prize in Chemistry.

Support for the symposia provided the opportunity to highlight the excitement of current chemical research, to educate the public about the achievements of chemistry and its contributions to the well-being of humankind.

The Principal Investigator is Professor Charles P. Casey of the University of Wisconsin-Madison, who was the 2010 Chair of the Chemistry Section of AAAS.

Statistical Mechanics of Defect-Mediated Dynamics in Complex Geomaterials

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Funding:	$175,000

We are investigating complex defect-mediated dynamics in the failure of rock masses, manifested in the nucleation and growth of defects, microcracks, damage, and macroscopic fracture. These processes are a result of the complex emergent dynamics of self-organizing geological materials which we are analyzing using the methods of statistical physics and large scale simulations, employing both molecular dynamics and Monte Carlo methods.

Understanding the physics of failure in rock masses is critical to the improvement of technologies in the areas of carbon sequestration, drilling, hydrofracturing for shale gas production, and storage of nuclear waste. Observations of rock masses over a range of spatial scales indicate that the failure modes of these systems, such as fracture, demonstrate scale invariant deformation, or power law behavior, characteristic of complex non-linear systems. These are observed in both laboratory settings in acoustic emission experiments as well as in large scale field settings. We are using statistical physics methods for interacting defect and damage fields, made possible by the construction and use of statistical field theories, to greatly improve our predictive capability for the macroscopic failure of materials. For example, driven threshold systems of rock masses in which defects interact with long range interactions display near mean field dynamics and ergodic behavior. This result, which was first proposed on the basis of simulations and theory, was subsequently observed in field observations on the tectonic scale.

We are employing computational simulations and statistical field theories for nucleation dynamics to (1) develop methods to determine the physical origin and dynamics of correlated statistical fluctuations and variability, as well as continue our studies on the lifetime of the material under load (the average time until failure); (2) compute the scaling properties of the statistical distributions and spatial clusters characterizing materials with damage; (3) determine the stability phase fields for deformation of these near-mean field materials; (4) compute correlation and response functions as an aid to understanding the emergent failure modes and space-time patterns of defects, damage, and fracture for geological materials under load; (5) develop statistical physics models including fully interacting defect and damage fields leading to correlated dynamics of systems with long range elastic interactions and near mean field dynamics; and (6) investigate and understand the hysteresis curves arising from deforming materials, comparing these especially to new data sets arising from Time of Flight analysis.

We are also employing the relatively new Monte Carlo techniques, such as the Wang-Landau algorithm and umbrella sampling, to allow us to simulate both larger samples and for longer times. In addition to providing greater insight into the problems discussed above, advances in the development of these new techniques are providing insight into a number of associated research problems that are of interest to DOE. These include phase transitions in materials such as polymers and metallic alloys and the evolution of damage in materials.

Thermodynamics of Minerals Stable Near the Earth's Surface

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Funding:	$246,000

The project “Thermodynamics of Minerals Stable Near the Earth’s Surface” 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 Earth’s “critical zone,” the near surface region of the planet most directly affecting and affected by human activity. The report of the 2007 DOE Workshop on Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems identifies as a Grand Challenge the “thermodynamics of the solute-to-solid continuum.” It identifies “nanoparticulate and colloid physics and chemistry” as priority research directions. This project continues to focus on these very issues. That is, 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) represent a continuous spectrum of events. The current grant has been investigating the energetic driving forces for such transformations and the new work expands these studies, with a strong emphasis on transition metals and redox reactions, especially involving iron and manganese oxides.

We will 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 now confident 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.

Multiphase Fluid Flow in Deformable Variable-Aperture Fractures

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Funding:	$124,000

Multiphase flow through fractured media is critical to many problems of interest to DOE including, CO_2 sequestration, nuclear waste isolation, and energy (petroleum and geothermal) production. In addition to the complexity introduced by multiple phases, these problems often involve deformation of the void space within fractures due to the influence of mechanical stresses and/or geochemical alteration of fracture surfaces. Rigorously predicting the influence of these often coupled processes is beyond the reach of existing continuum models used to simulate multiphase flow processes in fractured reservoirs. We are integrating quantitative laboratory experiments with the development and evaluation of mechanistic computational models of these coupled processes. Incorporating these single-fracture models into a large-scale discrete fracture network model, where the fundamental mechanisms are explicitly represented within individual fractures, will provide a comprehensive tool for evaluating the scaling of multiphase flow processes in deforming fractures. Results from these efforts will guide the development and evaluation of simplified constitutive relationships of these coupled processes.

Stable-Isotope Probe of Nano-Scale Mineral-Fluid Redox Interactions

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Funding:	$171,000

Stable isotope signatures can be used to interpret and model the physical and chemical history of metals in the environment. To accomplish this, it is important to understand how different process can generate different isotope signatures. The goal of this research program is to study how electron transfer processes at a reactive interface fractionate stable isotopes and apply our findings to understand isotope signatures arising from redox processes in a wide variety of natural environments. To unravel the different mechanisms for fractionating stable isotopes at a reacting interface, we have performed a series of electroplating experiments in which we have recovered the electroplated metal material, and measured its isotopic composition. By using electrochemical techniques, we can control the rate of metal deposition with simultaneous control of mass-transport to the electrode with a rotating disc electrode (RDE). This allows us to systematically study the competing effects of deposition kinetics and the mass-transport (diffusion) on stable isotope fractionation. We can also examine temperature- and time- dependent fractionation. These experiments allow us to address specifically the hypothesis that charge transfer kinetics drive a large fractionation of the stable isotopes of these metals relative to what is expected from calculated equilibrium fractionations.

We have performed isotope electroplating experiments on a variety of different metals, including iron, zinc, copper, and lithium. Results from all of these systems are qualitatively similar and show the following general observations. (1) In all cases the lighter stable isotopes of the metals are partitioned into the reduced metal species deposited on the electrode. (2) In many cases these stable isotope fractionations are larger than predicted equilibrium fractionation between likely species in solution and the metal phase. (3) Observed fractionation is found to be very sensitive to mass transport to the electrode, with much larger fractionations occurring when mass transport is fast (i.e., by using a fast rotation rate of a rotating disc electrode) and much lower fractionations observed when the electroplating process is clearly kinetically limited by mass transport to the electrode. The fractionation behavior is log-linear over at least four orders of magnitude of rate, for all systems. (4) Fractionation is also sensitive to temperature, with some surprising dependencies. When mass transport is the rate limiting step, the fractionation increases with increasing temperature. For all rotating disc electrode experiments, the fractionation decreases as temperature increases, as expected for isotope behavior. (5) Simple reservoir models using known governing equations for coupled electroplating-mass transport processes can explain *either* the overall electrochemical rates *or* the isotope behavior but not both simultaneously, given existing theories. Current work is underway to delineate the governing equations that are necessary to reconcile our rate and isotope observations.

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:	$155,000

The local water structure surrounding ions in aqueous solutions greatly affects their chemical properties such as reaction rates, ion association, proton and electron transport etc. We are developing the use of high-resolution XAFS observations and first principles based MD-XAFS (spectra simulated using first principle methods) to interpret the solution properties of strongly interacting aqueous solutes under arbitrary pressure and temperature conditions. In this period we analyzed new and published XAFS data for the series Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. In the first principle MD-XAFS method we are developing DFT based MD simulations are used to generate a large ensemble of structural snap shots of the hydration region. The simulations are based on a first principle evaluation of the electronic structure resulting forces. The structures obtained from the simulation are used in scattering calculations using the FEFF9 scattering code (widely used analysis tool for EXAFS calculations). The theoretical and observed scattering are compared and analyzed in terms of the structural detail from the MD simulation. Since all structure and multiple scattering pathways are included, the method provides direct information about the coordination numbers, the symmetry and the structure of the first and second hydration shells. Dynamical information is obtained in terms of the Debye Waller (DW) factors corresponding to various structural features of the scattering intensity.

The agreement between the calculated and theoretical data is remarkable. We would like to emphasize three important points about this novel approach to analyzing XAFS data. (1) The level of agreement between the calculated and observed amplitudes is considerably higher than the level that has been obtained by any XAFS analysis to date. (2) This was obtained from a parameter free simulation with no fitting to of the interaction potentials to any data. This supports the use of these methods for more difficult environments and more complex solutes (polyions). (3) New information about the shell structure is now available because of this more detailed agreement. We note also that both the multiple scattering and second shell features are well represented in the analysis. As far as we know, this is the first analysis of second shell structure and multiple scattering. In addition, because of the detail of this data, we have been able to evaluate both the accuracy of our pseudopotential representation of several ions and the level of accuracy of DFT approximations (PBE96 and PBE0) that are required to represent this data. The data is quite sensitive to the inclusion of core polarization in the pseudopotential. Hybrid DFT also provides a somewhat better agreement with the data. Remarkably the DW factors given by simulation are also in quite close agreement with the data. This is also the 1st time such agreement has been obtained. In order to obtain these result we had to develop efficient highly parallel computational methods for exact exchange and a QM/MM implementation. We have shown scaling with these algorithms to nearly 100,000 processors.

Fault-Related CO_2 Degassing, Geothermics, and Fluid Flow in Southern California Basins---Physiochemical Evidence and Modeling

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Funding:	$97,000

OBJECTIVES

This is a collaborative study to quantify basinal fluid flow, submarine methane migration, and diagenetic effects within deforming faults in a transpressional setting that is seismically active. The emphasis is on faulted basins in California.

PROJECT DESCRIPTION

We have mainly targeted active faults and young (Tertiary strata) petroleum fields in southern California for study. 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 the tectonic/diagenetic history and 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.

RESULTS

Our studies of the South Ellwood fault, which bounds the north edge of the offshore south Ellwood oil field, have given us direct evidence of connectivity between the sea bed and producing wells from changes in gas seep rate to the sea floor. Seepage of gas to the sea bed is influenced by well production approximately one kilometer beneath the sea bed. We estimate a 30 mD permeability for the fault zone from the rate of change in gas seepage at the seabed. Wells that appear to be in communication with the sea bed have elevated Mg contents although sulphate values are similar to other wells in the field. This may indicate relatively rapid reduction of sulphate from seawater. 87/86Sr values from these wells are higher than other wells in the field reflecting modern sea water values and contribution of elevated 87/86Sr values from the overlying formation.

A well in close proximity to the South Ellwood fault and one kilometer below the sea bed shows an ocean tidal signal pressure response during shut-in, indicating fluid communication with the ocean. We have successfully determined that the signal in the reservoir time lags behind the ocean tide by 7 hours. The signal strength (pressure) is attenuated by about 50% compared to the actual tide. From these data, we will calculate an independent measure of fault permeability.

In the LA basin, we have recently completed a preliminary Sr isotopic study of formation waters in the Long Beach field adjacent to the Newport-Inglewood fault zone. The results indicate the Sr values are highly radiogenic and significantly greater than expected Tertiary marine values. There appears to be significant differences across the field. The purpose of this study is to establish background water composition to evaluate possible upward fluid movement associated with the fault. Offset tubing strings and transient thermal anomalies indicate active fluid movement and a seismic creep along the fault in this area. Signal Hill Petroleum is planning a drill hole and core within the Newport-Inglewood fault zone. A recent 3-D survey of the prospective drill area is currently being evaluated with the plan to drill a test hole adjacent to the fault followed by drilling and coring through the fault zone. We anticipate that this project will provide a rich dataset for analysis of fault processes.

Our studies of rapidly precipitated carbonate shows that calcite precipitated at moderately fast rates and out of equilibrium (well scales, flowstone in tunnels) have oxygen isotopic values more positive that predicted from equilibrium. Carbon isotopic values can be very positive in well scales because of rapid loss of high proportions of CO_2 during degassing. Carbon/oxygen isotopic values co-vary with a positive slope between 1 and 5.

We are testing the hypothesis that during rapid crystallization, the light isotope is able to diffuse faster than the heavy isotope to the reaction site. In conjunction with collaborators at the University of Toronto, we are conducting a laboratory study of the effects of crystallization rates on carbonate stable isotopic compositions. Three types of experiments are being conducted, including mixing at different pH and CO_2 degassing. These experiments will be used to explain the extremely light oxygen isotopic composition of calcites we have observed in rapidly degassing environments such as well tubing scales and straw stalactite speleothems. We are also continuing to document carbonate isotopic compositions in rapidly crystallizing environments such as geothermal areas. These results are not predicted by conventional geochemical models, and they demonstrate the potential importance of metastable phases during CO_2 degassing and interpreting isotopic data from well scales. The work is relevant to sequestration and leakage of CO_2 gas from reservoirs.

Multiscale Investigation and Modeling of Flow Mechanisms Related to CO_2 Sequestration in Geologic Formations

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Funding:	$200,000

Multiphase flow in porous media is fundamentally a microscopic process that governs the behavior of geologic scale processes such as carbon dioxide sequestration in depleted reservoirs and saline aquifers, ground water hydrology, contaminant remediation, and enhanced oil recovery. The application of existing (standard) macroscopic models to problems of geologic scale multiphase flow has proved to be unsatisfactory within a wide range of governing parameters.

The relative importance of capillary, viscous, and gravitational forces acting on a large number of sharp microscopic interfaces separating the fluids, possibly in the presence of thermal gradients and chemical reactions, determine the overall flow characteristics which can involve instabilities at all length scales. Both the coupling of forces at the microscopic scale as well as the unstable nature of flow at various length scales cannot be modeled by the standard approach. This limitation severely impedes our ability to make accurate predictions regarding geologic flow, most notably in the area of carbon dioxide sequestration, which is a high priority mission area within DOE.

Our approach is to develop the missing link between the fundamental physics of multiphase flow at the pore-scale and the phenomenological representation of dynamic behaviors across a hierarchy of geologic scales. We will use the problem of CO_2 sequestration in geologic formations as a prototypical application of multiphase flow in porous media. We take this approach not only because of the lack of understanding of the sequestration process and its immense potential for environmental impact, but also because the process involves a wide range of fundamental physical mechanisms that arise in a host of other applications, such as contaminant transport and remediation as well as enhanced oil recovery.

Our objectives are to investigate the relevant physical mechanisms at the microscopic and mesoscopic scales with the help of detailed experimentation and high accuracy numerical simulations, as well as to carry out effective modeling of such mechanisms at the geologic scale based on the probability density function (PDF) approach. Our team of investigators represents a unique combination of experts who have driven progress in the areas of Level Sets-Ghost Fluid (Frederic Gibou) and stochastic multiscale methods (Hamdi A. Tchelepi) as well as developed innovative experimentation and visualization techniques for micromodels (Anthony R. Kovscek) and innovative and efficient Navier-Stokes solvers (Eckart H Meiburg). This team of researchers is therefore optimally positioned to achieve the objectives.

The proposed research will, in general, make it possible to make reliable predictions regarding geologic flows. In particular, it will significantly improve the understanding of hydrodynamic mechanisms and will allow the development of physically accurate macroscopic models in order to provide improved predictability and management capability for CO_2 sequestration and other geologic flows.

Canted Undulator Upgrade for GeoSoilEnviroCARS (Sector 13) at the Advanced Photon Source

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Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$205,000

GeoSoilEnviroCARS (GSECARS), a multi-user, synchrotron radiation research facility dedicated to earth, environmental and planetary science (Sector 13, Advanced Photon Source, Argonne, IL), is implementing a canted undulator upgrade in this project. The upgrade involves the addition of a second undulator to the GSECARS X-ray port with the two undulators installed in a canted geometry to provide two independent X-ray sources. One undulator optimized for lower X-ray energies (2.3-23 keV) will be the source for a unique sub-micron microprobe (next generation of the existing microprobe). This microprobe will be in a dedicated experimental station and will be used for detailed speciation and compositional research on both light elements (as low as sulfur) and heavy elements in systems of geochemical, environmental and cosmochemical significance. The magnetic array in the existing undulator will be replaced with one optimized for higher X-ray energies (5.6-80 keV) to significantly enhance the high-pressure and surface scattering research programs. Beamline modifications and component additions will also be made to allow independent utilization of the two undulator beams. The upgrade will double the amount of available undulator beam time opening up the capabilities of GSECARS to more investigators than currently possible. Because of the wide-ranging science program at GSECARS, the upgrade project is being supported through a division of costs involving DOE, NSF, and NASA. The Advanced Photon Source is providing the accelerator-associated components (undulator and front-end components).

GeoSoilEnviroCARS: A National Resource for Earth, Planetary, Soil and Environmental Science Research at the Advanced Photon Source

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Funding:	$815,000

GeoSoilEnviroCARS (GSECARS) is a national synchrotron radiation user facility for earth science research at the Advanced Photon Source (APS), Argonne National Laboratory. The APS is a 7 GeV storage ring producing extremely high brilliance X-ray beams using undulators, wigglers and bending magnets. The GSECARS sector, consisting of an undulator beamline and a bending magnet beamline, is operated by the Consortium for Advanced Radiation Sources, which is managed by the University of Chicago.

Synchrotron-based analytical techniques available at GSECARS include:

- X-ray fluorescence microanalysis with ~ 1 µm spatial resolution
- X-ray absorption spectroscopy including micro-spectroscopy and mineral surface analyses
- 3-D computed microtomography with micrometer resolution including transmission, absorption edge and fluorescence methods
- Inelastic x-ray scattering with ~ 1 eV energy resolution
- X-ray diffraction and spectroscopy in the diamond-anvil cell using both monochromatic and energy-dispersive techniques with double-sided laser heating apparatus. Online Brillouin spectroscopy is available on the bending magnet beamline.
- X-ray diffraction and imaging in the large-volume press using both monochromatic and energy-dispersive techniques using a 250-ton press on the bending magnet beamline and a 1000-ton press on the undulator beamline
- Powder diffraction, surface diffraction, and single-crystal microdiffraction

Principal research areas include (1) speciation and microdistribution of metals and radionuclides in soils, (2) redox reactions, transport processes and 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) crystal chemistry of rare, complex minerals, (9) dynamics of fluid transport in the subsurface, (10) equations-of-state of mantle phases, (11) rheology studies at high pressure, (12) determination of melting points and the densities and viscosities of melts, and (13) phase relationships in mantle minerals and candidate core materials.

A research environment is provided where users receive expert assistance in planning and conducting experiments and with data analysis. This service-oriented mode of operation allows the facility to be accessible to the entire spectrum of synchrotron radiation users from novices to experienced investigators. Beam time is available via peer-reviewed proposals submitted through the APS web-based proposal system. The APS web page contains calendars with proposal deadlines. The GSECARS web site (htttp://gsecars.org) contains valuable information for experiment planning.

Kinetic Isotope Fractionation by Diffusion in Liquids

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Funding:	$150,000

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. For this purpose 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 related 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. We have extended out earlier laboratory experiments on the thermal fractionation (also referred to as Soret diffusion in the geochemical literature) of the major elements (Si, O, Mg, Ca, and Fe) except for Al in molten basalt to now include the alkalis potassium and lithium. We find the alkali elements to be less fractionated by temperature differences than the major elements because of their faster chemical diffusion, which counterbalances the thermal effects. We are carrying out Soret diffusion experiments in water where we are reproducing Soret's original experiments for the thermal diffusion of dissolved salts (NaCl and KCl) and will measure associated isotopic fractionation of potassium.

We have also completed a study of magnesium isotopic fractionations associated with chemical diffusion of magnesium between melts of different composition exposed in the Vinalhaven Igneous Complex, Maine. Laboratory diffusion couples were made using rock powers from various rock types exposed in the complex to quantify the magnitude of magnesium isotopic fractionation by diffusion between these compositions when juxtaposed as melts. When the results of the laboratory experiments are compared to the magnesium isotopic fractionation associated with magnesium concentration gradients in the natural system, we find cases where the lab and field results are virtually identical; while along other profiles, there is no measurable magnesium isotopic fractionation associated with the magnesium concentration gradient. The degree of magnesium isotopic fractionation along a concentration gradient can thus be used to determine the relative importance of transport between melts by diffusion (which fractionates isotopes) and by mechanical mixing that does not fractionate isotopes.

Synchrotron X-Ray Microprobe and Microspectroscopy Research In Low Temperature Geochemistry

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Funding:	$209,000

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 (Upton, NY). 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 per square micron 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 oxidation state determinations used to infer the oxidation states of magmatic systems, and mineral surface controls on metal partitioning.

Physics of Channelization: Theory, Experiment, and Observation

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Funding: $65,000

This project seeks a fundamental understanding of the physical processes that erode channels and create drainage networks, by integrating theoretical models, laboratory experiments, and field observations. We focus on channels incised by groundwater flow, and we seek to quantitatively relate mechanisms of channel growth to channel shape and network geometry. Our studies of channel shape concentrate on the growth and form of elevation contours and longitudinal profiles. In order to investigate this problem, we performed laboratory scale experiments aimed at understanding the stability of an erosion front and its shape. Varying the geometry, the type of forcing (rain, seepage flow), and the type of material, we find that the erosion dynamics is highly dependent on how the eroded material is carried away. This aspect appears to control the stability of the front and may be responsible for the existence of an equilibrium position. Further, we have found that the erosion front does necessarily evolve in a straight line, and elongated eroded patterns resembling a channel are not observed. However, broad basins draining water are observed. The evolution of these structures is still unclear, but it could be related to the initial stage of the formation of a channel and is the focus of continued work. Our investigations are part of an integrative effort using physical reasoning, mathematical modeling, laboratory experimentation, and observations of kilometer-scale channels.

Correlating Mechanical and Electrical Properties of Rocks at the Sub-Millimeter Scale

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Funding: $156,000

At the mesos- and macro-scale, the connection between the elastic and the electromagnetic properties of granular materials such as rocks is not obvious and involves geometrical, chemical, and mineralogical effects. In previous work, we showed how to perform rapid near-field millimeter wave scanning to obtain high-spatial resolution maps of the spatially varying dielectric permittivity of rocks. In this project, we have extended this concept to laser ultrasound and we map the spatially varying mechanical properties of materials with similar resolution. We achieve this by using focused lasers to measure the propagation of ultrasonic pulses directly across "thin" samples. By comparing the spatially varying mechanical and electrical properties, we can see a clear correlation between the two at the submillimeter scale. There are practical implications of this work in area of climate change (since we can see annual variations in the organic content of sedimentary layers). This work also provides an experimental foundation for future theoretical work connecting elastic and electrical properties.

In the samples we have studied (including finely layered shales and medium grained granites), the dielectric contrasts have been larger than the mechanical. In particular, the dielectric permittivity of volatile organics is very low and shows up extremely well in the data. This makes for striking spatially resolved maps of the effects of pyrolisis as well as a rapid, noncontacting measure of the organic content (of both solids and fluids). Now that we have developed a reliable experimental methodology, we are turning to fundamental issues of the mesoscopic structure of rocks.

Multiscale Modeling of Dissolution in Rough Fractures

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Funding:	$92,000

Discrete fracture networks are widely used in reservoir modeling, because they provide an effective means to describe localized regions of high permeability. However, such models do not include the possibility that spatially localized dissolution can take place within an individual fracture in the network. However, in fractured carbonates, there is a universal instability in the dissolution front, which can reduce the breakthrough time in an individual fracture by orders of magnitude, thereby completely changing the hydraulic properties of the global fracture network. It is therefore important, in particular for applications to CO_2 sequestration, to develop a model of evolving fracture permeability that includes the inherent heterogeneity of the dissolution process. In this project, we are developing a multiscale analysis of the evolution of fracture permeability, using numerical simulations and linear stability analysis. Our simulations include fully three-dimensional simulations of the fracture topography, fluid flow, and reactant transport; two-dimensional simulations based on aperture models; and models of Laplacian growth.

Crystal Defects, Etch Pits, and Rough Surfaces: A More Complete Picture of Mineral-Water Interactions during Dissolution and Growth

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Funding:	$103,000

Our investigations in the current funding period focused on the following two aspects of carbonate formation: (1) template effect on the crystallization of Ca-CO_3 and (2) solvent effect on the precipitation of Mg-Ca-CO_3. The motivation to study template effect stems from the need to understand how silicates affect the nucleation and growth of Ca-Mg-carbonates in geological C storage media. In this area, we investigated calcite crystallization on biotite and pyroxene to determine the orientation relations between calcite and the substrates. In the other front, the inability for anhydrous Mg-CO_3 to precipitate at ambient conditions continues to pose a great challenge to geochemistry. We tested Mg-CO_3 crystallization in dry solvent methanol (MeOH) and formamide (FM), as well as MeOH-H_2O and dimethylformamide (DMF)-H_2O binary solvents. We hypothesized that (1) in dry conditions, the organic solvation shell is weaker than that of H_2O due to the steric effect of large or hydrophobic groups such as CH3 and (2) in binary system, organic molecules may substitute one or more solvation H_2O to distort and weaken the water cage.

Our results show that biotite has a strong controlling effect on the orientation of calcite nucleation. The primary orientation relationship between the growing calcite crystals and biotite substrate are calcite (001) ~//biotite (001) and calcite (010) ~//biotite (010). Our analysis indicates that calcite crystals initially nucleate from the Ca^{2+} layers and occupy the original K^+ sites on the biotite surfaces, followed by the attachment of CO_3^{2-} groups on the calcium monolayer to form the first unit cell of calcite. The geometry of this Ca^{2+} layer, which matches the calcite structure, could be the control factor on calcite a-axis direction. We found biotite substrate can enhance Mg incorporation into calcite as much as 19% $MgCO_3$ can observed in the calcite grown in solutions with Mg/Ca ratio of 5. Results from both natural and synthesized samples show that pyroxene (e.g., diopside) can also enhance epitaxial growth of calcite with preferred orientations between calcite a-axis and diopside c-axis. The observed large interface area between diopside and synthesized calcite indicate that the exposed Ca^{2+} and Mg^{2+} ions on surfaces with pseudo-hexagonal arrangements may serve as heterogeneous nucleation sites and, therefore, lower the nucleation energy barrier.

Numerous observations were made from a series of Mg-CO_3 crystallization experiments. (1) Precipitates are poorly crystallized or even amorphous in binary MeOH system. No anhydrous Mg-CO_3 was observed in pure MeOH at minimal water content. XPS results showed a likely formation of basic Mg-CO_3 phases. (2) Only amorphous $MgCO_3$ was observed in dry FA. FT-IR revealed that there was no H_2O or –OH in the precipitates. Further, for Ca-CO_3-FA system, well crystallized calcite and vaterite were observed. What's interesting is that when equal amount of Mg and Ca ions were present in the system, the only phase identified by XRD was dolomite. (3) Tri-hydrate Mg-CO_3 phase nesqhehonite was the only phase crystallized in the DMF-water binary solvent. It was found that after solubility correction, DMF accelerated the nesquehonite formation. Analysis of induction time showed the acceleration was not due to reduction of system energetic and likely resultant from a more rapid process of cluster aggregation.

Development of New Biomarkers for Surficial Earth Processes

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Funding:	$175,000

Numerous studies on multicellular plants have reported increasing carbon isotope fractionation with increasing concentrations of atmospheric carbon dioxide (pCO_2), but the magnitude of the effect is highly variable (i.e., 0.62 to 2.7‰ per 100 ppm CO_2). The majority of these experiments tested only small differences in CO_2 levels (<100 ppm), with maximum concentrations of elevated pCO_2 = 700 ppm. These studies conclude that carbon isotope discrimination [$\delta^{13}C = (\delta^{13}C[CO_2] - \delta^{13}C[plant])/(1000 +$

δ^{13}C[plant]) increases linearly as pCO_2 increases. A linear response suggests that the activity of RuBisCO, an enzyme fundamental to photosynthesis, is not limiting under any pCO_2 level. Such a conclusion further suggests that δ^{13}C will eventually exceed the enzymatic fractionation due to RuBisCO and that pCO_2 will be concentrated within leaves at levels greater than that outside the leaf. Because these conclusions violate fundamental understanding of photosynthesis, we conducted experiments within controlled growth chambers in which light, water, temperature, and relative humidity were maintained constant, and only varying the pCO_2 level under which plants grew. Two species of model plants, *Arabidopsis thaliana* and *Raphanus sativus*, were grown under 17 different pCO_2 levels ranging between 370 and 4200 ppm, in order to encompass the entire range of pCO_2 levels under which plants have evolved on Earth. From this large dataset of nearly 200 plants, we show that δ^{13}C is indeed a function of pCO_2, however, the relationship is hyperbolic, rather than linear, as is typically assumed. Across the small changes in pCO_2 previously studied, the response appears linear; however, our experiments across a very wide range of pCO_2 levels clearly shows that increases in δ^{13}C level off at high pCO_2, which is consistent with the ultimate control over fractionation being the activity of RuBisCO as the concentration of pCO_2 inside the leaf approaches the pCO_2 level outside the leaf. The response we measure indicates that changes in pCO_2 can affect δ^{13}C by as much as 7‰ across Geologic time, which is as great an effect as is measured among plants growing in desert to rain forest sites due to extreme variations in mean annual precipitation. Investigation of published data suggests that the δ^{13}C response to changes in pCO_2 is consistent across diverse plant types and our data show that the response is recorded in bulk below- and above-ground tissues, as well as n-alkanes, suggesting the potential for application to fossil plant materials in order to reconstruct pCO_2 across critical intervals.

Aqueous Geochemistry at High Pressures and Temperatures

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Funding: $100,000

This proposal outlines a plan for a program aimed at characterizing the physical nature of aqueous solutions at high pressures and temperatures. Research in this area has long been limited by the extreme experimental challenges and lack of data under the appropriate conditions. However, the vast majority of studies of aqueous geochemistry relevant to terrestrial problems of fluid-rock interactions have been conducted at 3 kbar or less and the widely used Helgeson-Kirkham-Flowers equation of state for aqueous species is applicable only at ~ < 5 kbar. These limits are unfortunate because fluid flow and reaction plays a central role in many deeper environments and higher pressure- temperature experiments could provide stringent tests of our understanding of the nature of aqueous solutions at high pressures and temperatures. Today, recent efforts, including our own, have resulted in new experimental techniques. These new techniques now make it possible to investigate properties of homogeneous and heterogeneous equilibria involving aqueous species and minerals over a much broader range of pressure and temperature appropriate for deep crustal and upper mantle processes involving water-rich fluids. We are carrying out (1) Brillouin scattering measurements of the equations of state and molar volume of aqueous solutions containing dissolved halide and carbonate species to at least 10 GPa and 700° C, (2) X-ray scattering experiments to constrain the structures of the same solutions, and (3) the phase diagrams of the aqueous systems. Progress will be optimized by collaboration among experimentalists at the University of Illinois Urbana-Champaign (UIUC), the Advanced Photon Source synchrotron (APS), and the National Synchrotron Light Source (NSLS). The proposed project is designed to facilitate such collaboration by bringing together investigators at the University of Illinois (Jay Bass) and partners at the GESCARS (APS) and NSLS beamlines. Experiments on fluid CO_2 will also be carried out at high pressures and temperatures to place constraints on the equations of state and phase diagrams under moderately extreme conditions.

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

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 addressed by this research included:

(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?

We performed a comprehensive analysis of how the communities of attached and suspended microbes in an aquifer vary depending on the geochemical composition of the groundwater, such as differences in sulfate and ferrous iron concentrations. Using microbial community profiling techniques, such as T-RFLP, our results show that the attached community reflects geochemical conditions better than the suspended. Specifically a statistical comparison of the community profiles reveals systematic similarities and differences in the bacterial communities between sites with high and low sulfate concentrations. We found no relationship of ferrous iron concentration to community composition in the aquifer, even where iron reducers seem predominant. Examining nearly full length 16S rDNA gene clones, we found bacterial populations associated with iron reduction on the sediment samplers we used, regardless of sulfate concentration or other obvious geochemical parameter, however their relative abundance dropped as the sulfate increased.

Integrated with our field investigation we 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. Our modeling work shows that in contrast to previous conceptual models, iron reducing and sulfate reducing metabolisms should coexist and even be mutually beneficial. The models show that communities assumed to be dominated by a single functional group may in fact be areas of mixed metabolism, and that zones containing iron-rich groundwater may be inhabited by sulfate reducing bacteria in a mutualistic relationship with iron reducers.

To address the kinetics of reactions we have also developed a molecular approach. As a test system we demonstrated that the gene coding for dissimilatory bisulfite reductase (dsr) was expressed at different levels relative to the rate of sulfate reduction. This theoretically could lead to a molecular approach to measure the gene expression in-situ to determine the rate of sulfate reduction. If successful, other gene targets could be developed that could provide kinetic information in groundwater systems.

Mineral-Fluid Interactions: Synchrotron Radiation Studies at the Advanced Photon Source

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Funding:	$65,000

The objective of this program is to advance the basic understanding of rock-fluid and soil-fluid interactions through experimental studies of molecular-scale processes at mineral-fluid interfaces. This is crucial to establishing the relation between molecular-scale processes and macroscopic geochemical transport in natural systems. Our principal approach is to observe single-crystal mineral surfaces in-situ during chemically controlled reactions with fluids using high brilliance synchrotron radiation. Experimental techniques include high resolution X-ray scattering (X-ray reflectivity, x-ray standing waves, resonant anomalous X-ray reflectivity) as well as X-ray reflection interface microscopy and X-ray absorption spectroscopy. Phenomena of interest include mineral-water interface structure, adsorption/desorption of ions and organic molecules, dissolution, precipitation and growth. Experiments are performed on common rock- and soil-forming minerals under conditions representative of geochemical environments near Earth's surface. A fundamental understanding of the molecular-scale processes is obtained through direct observations of interfaces before, during and after reaction, in parallel with thermodynamic analysis of solution-mineral equilibria, kinetic effects, atomic force microscopy, and molecular dynamic modeling.

The primary emphasis of these studies in the past year has been on understanding the reaction of mineral surfaces with solution species. The interfacial structure of calcite, effects of competitive ion adsorption, and the role of soluble natural organic matter in mediating ion-mineral interactions, as well as growth and dissolution processes, have been investigated at the calcite-water interface in the presence and absence of dissolved Pb and EDTA. Kinetics of uptake of Pb by the calcite surface have been measured, along with the interfacial structure of calcite as it evolves from surface incorporation through heteroepitaxial nucleation and growth of cerussite. Atomic force microscopy images provide corroborative information that aids in the interpretation of X-ray reflectivity data. In addition, we have continued to pursue similar studies at the muscovite-water and orthoclase-water interfaces. Systematic correlations of interfacial relaxations with adsorption of alkali ions at the muscovite-water interface have been characterized, as well as the relations between surface water adsorption, ion hydration, and ion adsorption at this interface. Dissolution kinetics at the orthoclase-water interface are being investigated as a function of solution composition using X-ray reflection interface microscopy with sub-micron lateral resolution. Spatially heterogeneous dissolution has been observed and its origin is being investigated.

Crystal Chemistry of Toxic Metal Sequestration

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Funding:	$200,000

This project centers on the crystal chemistry of minerals that host toxic metals in contaminated environments. The current focus is on the investigation of uranium sequestration by adsorption on surfaces and incorporation within mineral hosts using TEM, FIB, x-ray synchrotron and neutron scattering techniques.

Recent work has specifically focused on detailed study of a zirconium (oxyhydr)oxide phase discovered during our investigation of uranium contaminated sediments from the Hanford 300 Area vadose zone. Although Zr oxides, oxyhydroxides and phosphates have been extensively studied for use as U ion exchangers and to test applicability to remediation or prevention of contamination in soils and natural waters, this is the first such material recognized in a field setting. Characterizing this phase is complicated because it occurs in a variety of textures and is extremely fine grained. Even large aggregates of the material are intimately intergrown with phyllosilicates at the micron- to nano-scale in coatings on lithic and mineral fragments. Additional complications arise because of the overlap of x-ray peaks accessible in electron beam instruments. By integrating FIB, TEM-based EELS and electron microprobe analysis we have shown that the Zr material sequesters a significant portion (~16%) of the U in shallow vadose zone samples. We have also begun synchrotron studies including x-ray microprobe (XMP) mapping at the Advanced Photon Source (APS) beam line 13-IDC. The superior spectral resolution and accessibility of higher energy peaks in the XMP allow superior quantification of sample composition. We have also collected micro-XAFS (x-ray absorption fine structure) spectra and begun modeling to characterize coordination environments in the Zr-rich material

A second major thrust of our work has been the investigation of the basic crystal chemistry of meta-autunite group minerals. Our recent work on metatorbernite ($Cu(UO_2)2(PO_4)2 \bullet 8H_2O$) has emphasized the importance of understanding the structure of the interlayer region of the group as well as the controls on phase transitions between the lesser hydrates of the group. We have made substantial progress on these problems using electron, x-ray and neutron methods. This past year, we have designed experiments and collected the first data on activity-of-water versus temperature relationships for the lesser hydrates of metatorbernite. These experiments show that metatorbernite dehydrates reversibly to a phase with basal spacing of 8.3Å at temperatures as low as 76° C. We have also shown the formation of a 6.9Å phase at temperatures as low as 84° C. This transition is also reversible despite the fact that it involves a complete reconstruction of the autunite-type, uranyl-phosphate sheets to uranophane-type sheets. To elucidate interlayer details, we have also collected powder neutron diffraction data for deuterated metatorbernite and its first two lesser hydrates to probe the structural positions of water molecules in the interlayer. While that work continues, we are carrying out the first syntheses of deuterated meta-autunite in preparation for neutron scattering experiments on that Ca-bearing member of the group.

Predictive Single-Site Protonation and Cation Adsorption Modeling

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Surface complexation plays an important role in the equilibria and kinetics of processes controlling the compositions of soilwaters and groundwaters, the fate of contaminants in groundwaters, and the subsurface storage of and nuclear waste. However, there is no currently-available model of surface complexation that can be used to analyze these processes by predicting surface protonation and adsorption of metallic cations, anions and organic species for the wide range of fluid compositions, minerals, and temperatures and pressures that exist in nature.

Previous studies have shown that all the parameters in the extended triple-layer model (ETLM) can be predicted for alkalis and alkaline earths, enabling prediction of proton surface charge for oxides in 1:1 and 2:1 electrolyte solutions and mixtures of these. In current research, progress has been made over the last three years in extending the predictive ETLM for oxides to 1:2 electrolytes involving oxyanions such as carbonate as well as the adsorption of the oxyanions of silica. This enables surface chemistry calculations more relevant to natural waters than previously possible. Second, by applying the ETLM to oxyanionic organic acids such as glutamate it was demonstrated that prediction of surface species with the ETLM was consistent with measured ATR-FTIR spectra and quantum chemical modeling. Finally, it has become clear that electrolyte, transition, heavy metal and rare earth element cations prefer larger site densities than inorganic and organic oxyanions, which implies the need for a two-site model in order to treat natural waters that contain mixtures of cations and anions with a variety of valences.

Current work is continuing to develop the predictive capabilities and generality of the ETLM and expand the scope of previous applications; first by investigating the applicability of a two-site approach to simultaneous cation and oxyanion adsorption, second by developing an extension to higher temperatures, and third by developing a predictive model for oxyanion adsorption on all oxides. By so doing, the research aims to integrate the work of many experimentalists and to extrapolate to systems not yet studied experimentally and to natural and anthropogenically perturbed systems.

Collaborative Research: Evolution of Pore Structure and Permeability of Rocks Under Hydrothermal Conditions

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OBJECTIVE

The transport properties of rocks can be altered by diagenetic, metamorphic, and tectonic processes. Such changes are critically important to understanding 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. Simultaneous measurements of pore volume, permeability, axial, and volumetric strain rates will be made under isostatic and conventional triaxial loading. Temperatures (T) up to 800 K will be used, while confining pressure (Pc) and pore pressures (Pf) are maintained independently up to 500 MPa. Microstructure observation made with micro-CT, scanning electron microscopes, and laser confocal scanning optical microscopes will be used to quantify changes in surface roughness, porosity, and pore dimensions. The data will be used in network, finite-difference, and other numerical models to elucidate relations between permeability and other rock properties.

CURRENT RESULTS

(1) Progressive Microscopic Damage and the Development of Macroscopic Fractures in Porous Sandstones

We continue the quest to obtain quantitative relationship between microcrack damage and fault development during brittle failure in porous rocks. To investigate the interaction between progressive microscopic damage and macroscopic failure, we have conducted deformation tests on Darley Dale and Berea sandstones with initial porosity of 13% and 21%, respectively, in the brittle faulting regime. The novel aspect of our approach is to design a lateral relaxation compression loading configuration, in which the effective mean stress decreases as deviatoric stress increases. Dilatancy and strain softening were observed in all of the deformed samples. The critical stress at the onset of shear-induced dilation obtained under lateral relaxation compression is comparable to that reported for the conventional compression tests, but brittle failure during lateral relaxation loading was more stable, allowing us to investigate fault nucleation and growth and to measure quantitatively stress increment, strain softening, and dilatancy. Characterization of the progressive microstructural damage is conducted on a suite of samples deformed and subsequently unloaded at various post-failure stages. Recently, in addition to the lateral relaxation compression loading configuration, we also developed another loading configuration, in which we increases pore fluid pressure during damage accumulation and onset of brittle failure. This investigation is on-going.

(2) Effect of Temperature on Yielding Behavior of Carbonate Rocks

Permeability of porous rocks depends strongly on porosity and pore geometry, which can be substantially altered by mechanical and thermal loads. Knowledge of temporal and spatial variations in fluid flow, which is of critical importance to resource recovery, requires better understanding of the changes and the rates of changes of permeability and porosity at reservoir conditions. We deformed porous Indiana limestone samples with initial porosity of ~17% at temperatures of 298, 323 and 348 K under confining pressures ranging from 10 to 120 MPa. Simultaneous changes in permeability and sonic velocity were measured during deformation, as well as axial and volumetric strain, to track pore space evolution. Using our data, we have produced cataclastic flow yield envelopes that constrain the temperature dependence of compactive pore collapse and shear induced dilatancy in saturated carbonate rocks. We find that saturated samples show increased compaction and lower rock strength than dry samples and these effects are exacerbated by elevated temperature. Initial microstructural analysis shows that both dilatant microcracking and mechanical twinning play a role in the bulk behavior of the material. We suggest that increased water-weakening at elevated temperatures is the result of the interplay of crystal plasticity, microcracking, and pore collapse with chemically active pore fluid.

Collaborative Research: Evolution of Pore Structure and Permeability of Rocks Under Hydrothermal Conditions

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Funding:	$369,000

The broad objective of this proposal is to study changes in transport properties of rocks that result from mechanical deformation, structural heterogeneities, and low-temperature metamorphism using both laboratory and numerical experiments. Conventional triaxial mechanical tests are done at temperatures up to 700 °C and at confining and pore fluid pressures up to 400 MPa. Simultaneous measurements of permeability are done during the mechanical tests; and some experiments will also investigate the effects of concurrent metamorphism. Characterization of the pore space is done using SEM, confocal microscopy (LSCM), and CT microtomography. Numerical modeling using finite-element and finite-difference techniques also provides a powerful set of tools to understand variations in pore structure caused by compaction, diagenesis, and cementation.

Early Career - Nonequilibrium Physics and Phase-Field Modeling of Multiphase Flow in Porous Media

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Funding:	$150,000

Carbon capture and geologic storage, dissociation of methane hydrates in permafrost, enhanced oil recovery, and water dropout in low-temperature fuel cells all have something in common: two or more fluids flow simultaneously through a porous medium and the displacement of one fluid by another is often unstable (either due to gravity or viscous forces). Yet, our ability to model multiphase flow mathematically at the macroscale has remained a challenge. The traditional equations are unable to predict, explain, or even reproduce the formation of the complex patterns observed in experiments.

The overarching goal of this proposal is to develop a new continuum theory of multiphase flow in porous media following a phase-field modeling approach, which recognizes that the system is out of thermodynamic equilibrium.

We propose a radical new approach—phase-field modeling—to advance our fundamental understanding and predictive capabilities of multiphase porous media flow. The basic tenet, with origins in the mathematical description of solidification processes, is that the system is far from equilibrium and the energy of the system is a function of the inhomogeneous distribution of fluid phases in the pore space. This leads naturally to higher-order terms in the mass conservation equations. In recent work, we have used this formalism to develop a theory that explains and quantitatively predicts the formation of gravity fingers during infiltration into dry soil. The success of this application suggests that continuum models derived using the phase-field modeling framework have the potential to predict unstable multiphase flow in porous media.

The research agenda is organized around a set of hypotheses on hitherto unexplained behavior of multiphase flow. All of these hypotheses are nontrivial and testable. Indeed, a central aspect of the proposal is that we will test each of them by means of carefully-designed laboratory experiments, therefore probing the validity of the proposed theory.

Physics of Channelization: Theory, Experiment, and Observation

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Funding:	$187,000

This project seeks a fundamental understanding of the physical processes that erode channels and create drainage networks, by integrating theoretical models, laboratory experiments, and field observations. We focus on channels incised by groundwater flow, and we seek to quantitatively relate mechanisms of channel growth to channel shape and network geometry. Our studies of channel shape concentrate on the growth and form of elevation contours and longitudinal profiles. Our investigations suggest that the focusing of groundwater at the channel head selects predictable forms. We seek to better understand how these forms are selected. Bifurcations or ''tip-splitting'' of the channel head are of particular interest. At scales much larger than an individual channel, headward erosion, side-branching, and a succession of tip-splitting instabilities create channel networks. These processes are closely related to the ways in which subsurface water is attracted to channel heads. We seek a simple theoretical representation of the subsurface flow and attempt to relate it to sediment flux. Our investigations involve physical reasoning, mathematical modeling, laboratory experimentation, and observations of kilometer-scale channels. Our field investigations, performed at the Apalachicola Bluffs and Ravines Preserve near Bristol, Florida, emphasize quantitative tests of our theoretical predictions.

Rheological Properties of Earth's Upper Mantle at High Pressure: Roles of Melt, Water and Pressure

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Funding:	$90,000

Our project is an experimental approach to relevant Earth problems involving the flow of olivine-rich rocks in the Upper Mantle. 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.

We are undertaking three specific tasks. First, based on the recent observation that melt-solid dihedral angle decreases (i.e., wetting increases) with increasing pressure, we are investigating the viscosity of partially molten mantle rocks as the dihedral angle decreases toward 0 degrees with increasing pressure. Second, based on the increase in water solubility in nominally anhydrous minerals with increasing pressure (i.e., increasing water fugacity), we study the dependence of creep rate on water concentration at pressure-temperature conditions appropriate to Earth’s lithosphere as well as those appropriate to Earth’s asthenosphere. Third, based on significant improvements in stress resolution, we will measure the dependence of the viscosity of olivine-rich rocks on pressure (i.e., the activation volume, V*). Results to date have revealed a rather strong weakening effect that small amounts of water have on olivine-rich rocks, and a pronounced strengthening effect that increasing overburden pressure causes. We see indications that the magnitude of the pressure effect accelerates with increasing pressure, which suggests either a very strong or a very wet base of the Upper Mantle.

Computational and Spectroscopic Investigations of the Molecular Scale Structure and Dynamics of Geologically Important Fluids and Mineral-Fluid Interface

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Funding:	$189,000

PROJECT SUMMARY AND OBJECTIVES

The research supported by this grant focuses on development of molecular scale understanding of a range of critical issues related to the structure and dynamics of geochemically important fluids, fluid-mineral interfaces, and confined fluids using computational modeling and experimental methods. The work under this grant is closely aligned with the work undertaken under grant DOE DE-FG02-10ER16128 with the same title, Geoffrey Bowers of Alfred University, P.I. The Michigan State efforts are principally computational, and the Alfred University efforts are principally experimental.

PROJECT DESCRIPTION

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 surfaces is essential to understanding the fundamental chemistry of many geochemical processes relevant to energy geoscience. These processes include mineral reactivity, dissolution and precipitation, sorption, and geochemical transport. Our principal efforts are devoted to use of advanced computational approaches to address these problems, relevant experimental spectroscopic studies, and application of the computational methods to understanding the experimental results. The combination of computational modeling and experimental approaches is uniquely effective in addressing otherwise intractable problems.

RESULTS

In 2011, we initiated a series of computational studies of clay minerals and amorphous calcium carbonate (ACC). The work on clays studies the structure, dynamical behavior, and energetics of water and cations (Na^+, Ca^{+2}) in the interlayers and on the surfaces smectite (swelling clays), which are geochemically very abundant. These studies connect directly to the ^{43}Ca, $^{23}Na^+$, and ^2H_2O NMR studies of smectite by the Alfred group and are in excellent agreement with the experimental results. The results provide a molecular scale picture of the experimentally known differences between Na^+ and Ca^{+2} clays and also support the dynamical interpretations for water motion at surfaces developed from the NMR results. The computational results for amorphous calcium carbonate provide a basis for interpreting the ^{43}Ca NMR results for them and demonstrate that ACC pre-nucleation clusters in solution form rapidly and that previously published ACC structures with complex, heterogeneous atomic arrangements are stable.

Rheology of Earth's Interior: Experimental Investigation to Pressures of 15 GPa Using the Deformation-DIA

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OBJECTIVES

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 (i.e., water and melt). 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.

PROJECT DESCRIPTION

We have carried out a series of creep experiments on mantle rocks with emphasis on olivine, the major constituent mineral of the upper mantle, using a deformation-DIA (D-DIA), a solid-medium apparatus with the capacity of performing high-pressure triaxial deformation experiments.

Experiments were conducted at high temperatures (up to 1573 K) and high pressures (up to 10 GPa). Advanced synchrotron x-ray techniques enabled in-situ measurement of pressure, differential stress, and strain as a function of time. These data are used to quantify the flow properties of mantle rocks in terms of the dependence of creep rate on deformation conditions including stress, pressure, temperature, water fugacity, and melt fraction.

RESULTS

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 8 GPa and temperatures of 1373 to 1573 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. In the experiments, a cold-pressed cylindrical sample with a diameter of ~1.1 mm and a length of ~1.2 mm was encapsulated with 0.025-mm thick Ni foil and assembled with an alumina piston, a talc sleeve, and a graphite resistance heater into a 6.2-mm edge length cubic pressure medium. The enclosed talc dehydrates at high temperature, supplying water for sample during deformation. With the synchrotron x-ray beam, confining pressure and differential stress for a run are deduced from x-ray diffraction spectra, while the change in length of a deforming sample is monitored by a time series of radiographs. In our study, under hydrous conditions, samples deform about two orders of magnitude faster than under anhydrous conditions at the same differential stress, pressure, and temperature, demonstrating a significant influence of water on the viscosity of olivine. Specifically, our preliminary results illustrate that the creep of olivine depends on water fugacity at a power of ~2, which is about two times higher than that obtained at lower pressures ($P < 2$ GPa). More designed experiments are in progress to further delineate the flow behavior of olivine under hydrous conditions at high temperatures and high pressures; the result provides 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.

Evaluation of the Origin and Hydrocarbon Transport Capabilities of Solitary Waves in Fault Conduits with Visco-Elastic Rheologies

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Funding:	$125,000

The purpose of the present research was to characterize the origin and migration of solitary waves in elastic porous media, particularly within the geologic context of the Eugene Island minibasin, offshore Louisiana. The fundamental question addressed in the research was whether solitary waves can serve as a mechanism for enhanced hydrocarbon transport relative to the background compaction-driven flow regime. The solitary waveform is manifest as a zone of elevated fluid pressure and porosity that moves along the regional pressure gradient. Solitary waves are able to form when the rate of pressure generation at a location is greater than the rate of pressure diffusion, and when permeability is a sensitive function of effective stress, e.g., $k = k_0 \exp(-\sigma_e/\sigma^*)$, where k is permeability, k_0 is permeability at zero effective stress, σ_e is effective stress, and σ^* is an empirical parameter that represents the influence of compaction on permeability. Pressure generation rate in the hypothesized hydrocarbon source sediments at Eugene Island was calculated via a two-dimensional numerical model using the BasinMod2D™ software. This model reconstructed the 3.6 million year depositional history of the Eugene Island minibasin, calculating in coupled fashion the compaction of the sediments, resulting changes in their porosity and permeability, temperature, fluid pressure, and the production and flow of hydrocarbons and water. Results of the modeling showed fluid pressure in the source sediments to increase at an average rate of about 30 Pa/year, resulting in overpressures of about 55 MPa above hydrostatic pressure by the present day. Approximately 90% of this overpressure was found to be caused by compaction disequilibrium, with the remainder caused by hydrocarbon generation.

The pressure generation rate determined from the BasinMod™ calculations was used as input in a separate model that solved the continuity equation for a single fluid phase consisting of oil using an implicit finite difference method over a five kilometer vertical profile. The calculations showed that solitary waves were only able to form over a narrow permeability range of about $\log k = -24$ to -25 m^2. For permeabilities greater than $\log k = -24$ m^2, fluid pressures diffused too rapidly from the source region for a coherent wave to form. For permeabilities lower than $\log k = -25$ m^2, the solitary wave grew to a large amplitude but was effectively immobile over the 3.6 million year lifespan of the Eugene Island minibasin. Solitary wave formation and propagation required high initial fluid pressures in the range of about 90-95% of lithostatic pressure. When fluid pressure lay outside of this range, as a result of the permeability-effective stress relationship noted above, permeability lay outside of the $\log k = -24$ to -25 m^2 range such that solitary waves either did not form or formed but did not move from their source location. As solitary waves ascend, their amplitude diminishes and they leave behind a wake of slightly elevated fluid pressures (typically 1-2 MPa above the initial background values) that increases the permeability enough to prevent further solitary waves from forming. Thus, for time spans on the order of the 3.6 million year history of Eugene Island, solitary waves would not form in succession, which limits their hydrocarbon transport efficacy. Solitary waves were only able to ascend 1-2 kilometers from their source regions before their amplitudes diminished to background fluid pressure and porosity values. As they ascend, their velocity increases from order 0.1 mm/year to order 1 mm/year. Wave volume was found to increase during the early stages of ascent, peaking after a travel distance of about 0.5 to 1 km at a pore volume of about 0.001 km^3. Thus, solitary waves are unlikely to have charged the shallow Pleisocene reservoirs at Eugene Island with oil, though it is possible that solitary waves could be important agents of oil transport in other locations where the reservoirs are more proximal to the source rocks.

A New Probe for Understanding Rock Elasticity - Time of Flight Modulation

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The velocity of an acoustic pressure or shear wave through a medium is determined by its elastic constants. If those "constants" are functions of the local strain, then nonlinear effects (e.g., distortion of waveforms hysteresis and dispersion) will occur due to strain variations caused by the propagating wave itself. In porous rocks such as sandstones, these effects can be very strong at low strains and are relevant to seismic velocity measurements and the mechanical effects of removal of oil and gas, and replacement of water, brine, or carbon dioxide into the pores.

We use acoustic methods to determine the wave velocities and elastic behavior of laboratory samples as we change the strain state by temperature, pressure, or chemical environment changes. The detailed response of resonances in the rock and the direct measurement of wavespeed through wavepacket time-of-flight (TOF) records during these strain modulations (hence TOFM) are our tools. Resonance methods are quite well developed; TOFM is a new tool being developed with collaborators at the Los Alamos National Laboratory.

We have a Berea sandstone rock core instrumented with piezoelectric transducers for both resonance and TOFM measurements, isolated in a stainless steel chamber, where we can change the chemical species (as gas) present, the temperature, and the overall pressure. Currently we are limited to a few atmospheres of high pressure, but can produce good vacuum environments. We are pursuing the influence of water and carbon dioxide under the idea that the silica cementation and overgrowth are high strain regions under deformations and that microcracking, grain boundaries and structure (e.g., is there amorphous silica present?) can link local chemistry to bulk mechanical elasticity there. This project support started recently (August 2011), but we have initially attempted to remove water from the sample by evacuation and heating. We have the driest sandstone on Earth – the vacuum is 1 nanoTorr at room temperature. When we heat this very dry rock, we see a dramatic decrease in nonlinearity and Q of the sample, reproducibly at the rather low temperature of 40C. This did not occur with the humidified sample. The feldspar and clay content of Berea sandstone (amounting to about 15% of the mass, remainder silica) are also influenced by water removal, but the silica grains and cementation still represent most of the mechanical structure of the sandstone. We will be presenting these results at the 2011 AGU fall Meeting (R. Miller et al.) and hope to be able to add information on this transition as argon gas (no chemistry, but about the same mass as carbon dioxide), carbon dioxide, and water vapor are reintroduced to the rock.

The identification of the microscopic (grain to sub-grain size) elements responsible for the nonlinear effects we observe with acoustic probes will enable improved geophysical/geochemical prediction of seismic and bulk structural effects, and extends into broader material arenas like non-destructive testing.

Complex Fluids in Self-Affine Fractures

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Funding: $96,000

Naturally fractured rocks have “self-affine fractal” surfaces which exhibit power-law correlations, giving rise to distinctive velocity fluctuations and transport inhomogeneities when fluids or tracers pass through the fracture. The goal of this research is to understand (1) the interplay of diffusion and convection in the hydrodynamic dispersion of non-Newtonian liquids and (2) the evolution of the fracture surface when (non-colloidal) particulates carried by the fluid deposit on the walls. Both problems are characterized by nonlinear feedback mechanisms, which renders their analysis difficult. In the first case, the velocity variation within a heterogeneous fracture leads to an inhomogeneous shear stress pattern, which in a shear-thinning liquid, causes spatial variations in viscosity, which enhances the velocity variation. In the second problem, deposition processes alter the fracture geometry, which in turn alters the velocity and stress fields, which can then promote or discourage deposition in different regions of the fracture. We will employ numerical simulations based on the lattice-Boltzmann method, based on our newly developed codes for shear-thinning liquids and solid particle transport, complemented by effective medium and other averaging techniques.

Stress-dependent Acoustic Propagation and Dissipation in Granular Materials

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Funding: $123,000

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.

Changes of Porosity, Permeability and Mechanical Strength Induced by Carbon Dioxide Sequestration

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Funding: $210,000

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 parameters such as partial pressure of CO_2, pH and cation concentrations of the brine, temperature, and advective velocity will be investigated.

(2) Correlation of porosity and permeability changes to before-and-after changes in the sample microstructure. The microstructural changes will be characterized via X-ray computed microtomography.

(3) Measurement of mechanical properties of the limestone and sandstone samples that have been altered by injection and percolation of CO_2, with the objective of understanding how mechanical failure is influenced by modification of the pore space.

Progress to date on these three tasks are summarized below.

(1) The flow-through experiments are pursued in the aqueous geochemistry lab of Professor Martin Schoonen. Our investigation requires significant modification of preexisting equipments in the Schoonen lab and incorporation of some components from Wong’s lab. We have made progress in setting up the necessary apparatus for this task. In response to critical suggestions from reviewers of the proposal, we will first focus on carbonate rocks, namely the Tavel and Indiana limestones.

(2) A major challenge in characterizing the pore geometry of carbonate rock is its complexity; depositional environment and diagenesis exerts significant genetic influence over the development of texture and fabric of a carbonate rock, which can in turn modify both the size and connectivity of the pore space in a relatively rapid and drastic manner. The pore size in a carbonate rock may span over a very broad range, with a distribution that is often bimodal, including a significant subset of microporosity that may not be resolvable using microtomography. With reference to microtomography data for several porous limestones, we have made advances in segmentation of their pore spaces into macro- and micro-pores, and are in the process of characterizing geometric attributes such as pore size, specific surface area, and connectivity.

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 model for highly caustic solution flow through unconsolidated soils typical of the Hanford site. There is a high likelihood that carbonate cap rock will be encountered in realistic scenarios of CO_2 sequestration; the need for an accurate understanding of in-situ reaction rates can be addressed through the type of network flow models we can build.

(3) 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. In Wong's lab, previous investigation of carbonate rock deformation has focused on nominally dry sample, and published data on water-saturated samples are not always in agreement. In our investigation, we have begun to isolate the chemical and mechanical effects.

Reactivity of Iron Bearing Minerals and CO_2 Sequestration: A Multi-Disciplinary and Experimental Approach

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Funding:	$79,000

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) contacts 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 deep saline formations. A representative suite of well-characterized sedimentary rocks (sandstones, siltstones, marls, and carbonates) will be exposed to $scCO_2$, $scCO_2/H_2S$, $scCO_2/SO_2$ 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 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. These studies concentrate on iron bearing minerals common to sandstone.

Multiscale Modeling of Multiphase Flow, Transport, and Reactions in Porous Medium Systems

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Our work is aimed at advancing the thermodynamically constrained averaging theory (TCAT) approach for constructing models of multiphase porous medium systems at a range of length scales. By this method, all variables are expressed in terms of explicitly defined averages of microscale properties; and closure relations are constrained to ensure conditions consistent with the second law of thermodynamics. The results of this approach are models that can be constructed at a range of length scales, explicit definitions of all variables in terms of microscale precursors, hierarchical families of models that vary in sophistication that can be matched to a physical system of concern, and assurance that the models derived are thermodynamically constrained and consistent. This work involves a theoretical component to formulate candidate models, a pore-scale modeling component to guide the formulation of specific closure relations, and a continuum-scale numerical methods component to approximate the formulated macroscale models.

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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OBJECTIVES

To better understand electron transfer reactions between FeII in minerals and sorbed polyvalent metals such as UVI. To develop ab initio models for the XPS and XANES metals in order to help elucidate information on oxidation states and bonding environments.

PROJECT DESCRIPTION

We are exploring the influence of the U coordination environment on the reduction of U(VI) to U(V) to U(IV) at the ferrous mineral-fluid interface. Key experimental techniques used are electron microscopy, x-ray photoemission spectroscopy (XPS), and x-ray adsorption near edge structure (XANES). This summary describes the theoretical efforts in the project that are directed toward the quantification of the chemical interactions between U and O from the analysis of core-level spectra. We are concerned with how these chemical interactions may be different depending on the formal U oxidation state. The objective of the theoretical analyses of XPS and XANES spectra is to enable us to extract from the core-level spectra information about the influence of the coordination environment.

RESULTS

Our theoretical efforts in the present year have focused in three broad areas. First, we have made the first fully ab initio analysis of the 4f XPS of U(VI) in UO_3 where full account has been taken of the U-O chemical bonding. Second, we have examined the vibrational broadening of XPS peaks in new cases and shown that this broadening does reflect the materials chemistry. The effect for Ceria, a lanthanide oxide, has been shown to be small because of an unexpected consequence of the XPS closed shell screening. Third, we have made major advances in our computational capabilities. These advances, and further efforts planned for the coming year, will allow us to move beyond the systems we have treated thus far.

For the XPS spectra of U(VI) in UO_3, we have developed a materials model of an embedded UO_6 cluster and an electronic structure model that takes into account many body effects through the mixing of XPS allowed with XPS forbidden configurations. The forbidden configurations have a shake origin where the outgoing core electron excites a valence electron from a bonding into an anti-bonding level that is close in energy. We have compared our theoretical and experimental 4f XPS spectra for UO_3. The theory reproduces the main peaks and ~4 eV satellites. Our theory allows us to quantify that the main peaks have lost 35% of their intensity to the shake satellites and our many body treatment has recovered all but 8% of these losses. The losses arise because of the closed-shell screening. Our theoretical analysis shows that when the 4f shell is filled, the chemical bonding between the U(5f) and the O(2p) orbitals leads to an effective occupation of the U(5f) orbitals by 1.4 electrons. For the 4f-hole configuration, the screening increases the U(5f) occupation to 2.6 electrons. The change of 1.2 electrons in the occupation of the 5f orbitals shows that the core-hole is over screened by the covalent interaction. A similar over-screening occurs for the XPS of Ce in CeO_2 and the consequences for vibrational broadening are considered below.

We have studied the vibrational contribution to the exceptionally large broadening of the Ceria XPS. In contrast to more ionic oxides, where the vibrational broadening is quite large, the vibrational broadening is negligible for the XPS of Ceria. This difference can be understood because for CeO_2 and UO_3 the large closed shell screening, described above, reduces the electrostatic forces that drive the vibrational excitations. We are now in a position to determine the importance of vibrational broadening for different oxidation states in UOx.

Major progress continues to enhance our codes so that we can extend our studies to complex oxides and extend our many-body treatments to allow us to relate XPS satellites to their origins in chemical interactions. We have restructured the arithmetic used in our calculations so that we can handle very large collections of numbers. In effect, this means that we are no longer limited to including only 16,000 terms in our many body treatments but we can now treat objects where there are a billion terms; the limitation that had prevented us from making quantitative studies of the satellites structure in open shell oxidation states of lanthanides and actinides has been removed. However, since the time to solve the many body equations increases to the third power of the number of many body terms, we are in the process of parallelizing the solution of these equations. Our initial tests on dedicated workstations show that we can gain an order of magnitude in the elapsed time to solve these equations. With the additional resources available at supercomputer centers, we expect, at least, a further order of magnitude improvement in the solution times. We are also developing programs to determine the extent to which the spin-orbit splitting in actinides reduces the net spin moments of these systems. These new programs will allow us to determine the average spin orientation of an actinide cation and determine how much it is reduced from the ideal non-relativistic values where spins are assumed to be parallel to the greatest extent possible. This capability will allow us to study departures from the magnetic and chemical properties expected for systems when the spin-orbit splitting is not taken into account. While these enhancements have been implemented on our proof-of-concept code, we expect in the coming year to work with our EMSL partners at PNNL to port this code on supported platforms to improve its ease of use and its accessibility. Other enhancements are planned for the coming year to improve our treatment of symmetry and our use of pseudopotentials to allow us to treat several heavy atoms. When this is completed, we will have a world class, user friendly code that will allow the reliable, quantitative analysis and interpretation of core-level spectra.

Metal-Anion Pairing at Oxide/Water Interfaces: Theoretical and Experimental Investigations from the Nanoscale to the Macroscale

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Ion adsorption and the potential formation of ternary complexes on silica (quartz, amorphous silica), alumina (corundum and gibbsite), and ferric iron (goethite and hematite) oxides are under investigation. Our studies have focused on systems involving alkaline earth metal (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) and heavy metal (Co_2^{2+}, Cd^{2+}) cations. The anions we have selected for study include $Cl^{-,}$ NO_3^-, ClO_4^-, SO_4^{2-}, SeO_3^{2-}, and SeO_4^{2-}. This collaborative project combines the use of several techniques including bulk adsorption experiments, X-ray absorption (collaborator Katz), infra-red, vibrational sum frequency generation, and total internal reflection Raman spectroscopies (XAS, IR, VSFG, TIRR), and molecular modeling (collaborator Criscenti) to investigate ion adsorption at mineral surfaces. XAS provides data on how the metal binds to the surface (e.g., monodentate, bidentate), IR provides data on bulk anion adsorption at mineral surfaces from aqueous solution, and VSFG and TIRR provide surface data on anion adsorption at the mineral surface as well as impact of adsorbed metal-anion pairs on water structure at the mineral surface. Research taking place in our laboratory during FY2011 primarily focused upon: (1) VSFG investigations of sulfate adsorption to hematite coated CaF_2 and CaF_2, (2) the development of a TIRR spectrometer for the study of SeO_3^{2-} and SeO_4^{2-} adsorption to the ferric iron oxides of interest, and (3) preliminary investigations into the interactions between adsorbed anions and several cations of interest (Mg^{2+}, Co^{2+}, and Cd^{2+}). The current VSFG studies on CaF_2 indicate that sulfate primarily adsorbs to the mineral surface as a bi-dentate inner-sphere complex with a surface free energy of adsorption of approximately -30 kJ/mole. Initial measurements on hematite coated CaF_2 indicate adsorption characteristics similar to what is observed with bare CaF_2. Development of a working TIRR spectrometer allows for analysis of anion vibrational modes and therefore the study of SeO_3^{2-} and SeO_4^{2-} adsorption.

An Investigation of Roughness and Weathering at the Bedrock-Regolith Interface

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The depth profiles of chemistry and texture written in weathered regolith comprise a textbook that records the rates of biogeochemical processes and manifests the fractal nature of the bedrock-regolith interface. Unlike a Euclidean planar interface, the fractal weathering interface has a “thickness” or roughness that varies with the scale of measurement. The roughness can include both undulations on a "planar" interface or particles. Given its fractal character, the area of this interface is a function of both the roughness (root mean square, RMS) and the complexity (fractal dimension) of distribution of these features. One of the reasons that area-normalized weathering rates in the laboratory differ from rates in the field is that roughness and complexity of this interface varies at different scales of measurement and are difficult to quantify.

For example, it is obvious that the RMS roughness of a weathering mineral-water interface measured at the atomic scale is smaller than that of the core-rind interface of a weathering clast. The latter includes roughness contributed by undulations in the weathering surface due to individual grains or fractured surfaces within the clast, and these undulations are not measurable at the atomic scale. Similarly, the roughness of the bedrock-regolith interface is larger when considered at the pedon and landscape scales because it includes even larger vertical asperities contributed by fractures or faults. It is less obvious how the fractal dimension of the weathering interface varies with scale. In this project, we have hypothesized that we can use insights about the fractal character of surfaces gleaned from model crystal and rock simulations to extrapolate weathering advance rates and reaction front thicknesses across scales. To learn to do this, we are making both model simulations and observations of systems chosen to interrogate the effect of lithology, climate, hillslope curvature, and hillslope position.

Specifically, we are (1) analyzing chemistry, mineralogy, particle size, microbiology, and neutron scattering in weathered systems on samples from three lithologies chosen at mineral surface, clast, pedon, and hillslope scales; and (2) comparing the observations to models of weathering to interpret weathering rates and the weathering interface.

The Physics of Swarms in Fracture Networks: Integration of Seismic Characterization and Controlled Micro-Transport

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OBJECTIVES

The objective of this research is two-fold: (1) determine how to control the injection and retrieval of simulated sensor swarms within fracture networks and (2) determine how to detect, seismically, the dominant flow path through fracture 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.

PROJECT DESCRIPTION

A laboratory study was performed to explore the evolution, maintenance, and control of swarms in fractures. Fractures with a uniform aperture and with a converging aperture were used to test the effect of fracture aperture on swarm behavior (0.5 mm up to 50 mm). Swarms were composed of water and either Soda-Lime glass (25 µm diameter, hydrophyllic) or Polystyrene (3 µm diameter, hydrophobic) beads in 1-2% solutions. A swarm was released into the fracture via a pump-driven hypodermic needle set to produce a swarm volume of 5μL. After release, the swarm fell under gravity and was imaged with a CCD camera at 5 frames per second.

We also studied the use of fracture interface waves to interrogate the properties of fracture intersections. Experiments were performed on an aluminum sample with two orthogonal intersecting fractures. A seismic array was used to propagate compressional (P) and shear (S) waves (central frequency ~1 MHz), through the sample for a range of normal stresses (1.4 to 14 MPa). The sample was subjected to either uniaxial or biaxial loading without de-coupling the transducers from the sample. Measurements were made for S-wave polarizations that were parallel and perpendicular to each fracture and the fracture intersection.

RESULTS

Swarms in Fractures. Fracture morphology and particle hydrophyllicity/hydrophobicity play a strong roll in the formation, evolution, and breakup of particle swarms. Fracture walls produce two competing mechanisms that affect swarm velocity and evolution through bifurcation in fractures, namely drag and confinement. From our experimental results, we find that the behavior at small apertures (less than the swarm diameter) is dominated by fluid drag that slows the swarm. In intermediate apertures (less than 10 times the swarm diameter but greater than the swarm diameter), the swarm is dominated by wall confinement that prevents the swarms from expanding and thus maintains the swarm particle density and swarm velocity. For apertures greater than 10 times the swarm diameter, the fracture exerts minimal influence on the swarm, allowing it to propagate as if through an open water. For the converging fracture, the swarm traveled through a high aperture region before it reached a uniform aperture fracture. The particles have sufficient time to expand and to lose their cohesion before reaching the highly confined region of the parallel fracture. The resulting swarm speeds prior to bifurcation are similar for both the uniform fracture, at 50 mm, and the converging fractures for apertures, from 8-20 mm.

Fracture Intersections. The existence of fracture intersections is a major difference between working with single fractures and orthogonal fracture sets. Compressional and shear waves were propagated along fractures as well as along an intersection for a range of normal stresses (1.4 MPa to 14). At an intersection, the bulk shear was quenched and the existence of interface waves was independent of the polarization of the shear wave source. These intersection waves were observed to be highly sensitive to stress concentrations along the intersection, including the orientation of the applied stress. The measured velocities were used to estimate the stiffness of the fractures and the intersection based on the theory for generalized Rayleigh waves. For a single fracture, the stiffness remained roughly constant, while the stiffness along the intersection did not. The intersection stiffness was found to either increase or decrease with load, depending on the polarization of the seismic wave and the loading condition. The velocities of the interface waves on the intersection were found to fit the predicted range of velocities only for certain polarizations and loading conditions. This is the first evidence that the behavior of waves propagating along an intersection is more complicated than that of fracture interface waves. Intersection waves have the potential to provide a powerful tool for monitoring both mechanical and hydraulic properties of fracture intersections.

Grain-Boundary Transport of Incompatible Elements in Rocks

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The textural and compositional evolution of polycrystalline rocks is strongly controlled by an intricate set of kinetic feedback mechanisms that operate along grain boundaries in rocks. In systems that lack a wetting fluid or melt, transport of elements must occur by diffusion along pathways composed of 'dry' grain boundaries and grain edges. Since grain-boundary diffusion is commonly 10^4 to 10^6 times higher than diffusion through the lattices of most rock forming minerals, rapid transport of components through low volume grain boundaries may govern the kinetics of textural and geochemical equilibration. Grain boundaries also act as important geochemical reservoirs because elements that are incompatible in the dominant matrix minerals of a rock are partitioned into grain boundaries. The geochemical evolution of rocks can be strongly affected by grain-boundary diffusion and partitioning processes, which can induce elemental and isotopic fractionations similar to processes that modify compositions in mineral/melt and mineral/fluid systems.

Experiments were conducted to study grain boundary diffusion of the elements Mg, Fe, Ni and Mn in dry quartz grain boundaries. Type-C diffusion kinetics controlled transport because the elements are incompatible (i.e., insoluble) in the quartz crystals adjacent to the grain boundaries. Because the incompatible elements were confined exclusively to the ~1 nm grain boundaries, diffusant transport was measured using the detector particle method. The two-step procedure involved synthesis experiments followed by the diffusion experiments themselves. Quartzites containing fayalite (Fe_2SiO_4) and enstatite ($MgSiO_3$) detector particles were synthesized at high P-T conditions in a piston-cylinder apparatus to produce rocks with equilibrium microstructures. After synthesis experiments, the rock analogs were cut into disks and polished. In the diffusion experiments, polished surfaces of the rock analogs were placed against polished disks of Mg-, Ni- and Mn-rich source materials (MgF_2, MgO, or Mn metal containing Mn) to induce chemical potential gradients and incompatible element transport.

Two different configurations were used for grain boundary diffusion experiments. Standard-type detector particle experiments were conducted by placing the fayalite- and enstatite-bearing quartzites directly against polished disks of the source materials. The only pathway for transport from the diffusant source to the detector particle sink minerals was along the grain boundaries. The detector particle diffusant contents decrease as a function of distance from the quartzite/source interface. A time series of experiments demonstrate that the detector particles of relatively large volume that reside closest to the diffusant-rich source act as 'infinite sinks' and incorporate all the diffusant supplied by the low volume grain boundaries. Thus the longest experiments from the time series do not show significantly greater transport distances, but the detector particles closest to the source have higher diffusant concentrations.

The effect of detector particle abundance on diffusive length scale of Ni and Mn was examined in experiments with quartzites that contained 1-4 wt% enstatite. The diffusive length scales of Ni and Mn are substantially longer in rocks with lower abundances of detector particles. These experiments also allowed us to evaluate how partitioning of diffusants into detector particles may cause elemental fractionation. Enstatite preferentially partitions Mn over Ni. Consequently, Mn will be sequestered in detector particles while Ni 'prefers' to reside in grain boundaries where it can be rapidly transported by grain-boundary diffusion. The results demonstrate that grain-boundary diffusion induced fractionations may produce rocks with variable mineralogy and composition.

The second type of grain-boundary diffusion experiments used sandwich-type configurations composed of monomineralic quartzite slabs sandwiched between MgF_2 and a quartzite containing fayalite detector particles. The sandwich-type experiments were designed specifically to evaluate Fe-Mg transport in quartzite grain boundaries. The uptake of Mg by the fayalite detector particles imbedded in the quartzite confirms that Fe-Mg exchange occurred through the dry grain boundaries of the intervening quartzite. During the diffusion experiments on initially monomineralic quartzites, pyroxene crystallites (up to 5 µm) grew along the grain boundaries of the intervening quartzite. The new pyroxene crystallites nucleated as Fe-Mg exchange along the quartz grain boundaries supplied the necessary components to form these crystallites. The Fe and Mg contents of the crystallites vary linearly across the entire width of the quartzite, suggesting that steady-state transport conditions were rapidly established. At 1125°C a grain boundary flux of 1.48×10^17 atoms Fe/m2s was determined from the uptake of Fe in the MgO source material from the standard-type experiments, and a grain boundary flux of 1.78×10^20 atoms Mg/m2s was determined from the uptake of Mg in fayalite detector particles in sandwich-type experiments. Assuming that steady-state conditions prevailed during the experiments, we estimate grain boundary diffusivities for Mg and Fe in dry quartz grain boundaries to be ~10^-10 and ~10-^-14 m2/s, respectively.

Framework for Constitutive Branching in Porous Rocks Undergoing Brittle Faulting and Cataclastic Flow

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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 are developing a mesoscopic scale modeling approach to investigate the interplay between these two fine-scale processes as they impact pore collapse. We are modeling the solid matrix microstructure using the finite element method with the voids represented by hollow inclusions. Grain crushing is represented by multiple slip surfaces through the solid matrix, and irreversible deformation in the mineral grains is modeled using crystal plasticity theory. An extended finite element (FE) formulation is being 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 are being 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 can conduct a bifurcation analysis at the mesoscopic scale to investigate pore collapse instability at that scale. Laboratory-measured specimen responses are interpreted in the context of instabilities occurring in the mesoscopic level.

Multiscale Investigation and Modeling of Flow Mechanisms Related to CO_2 Sequestration in Geologic Formations

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Micromodel drainage experiments of immiscible two-phase flow were performed. The viscosity ratio (M) varied from highly favorable (M = 0.3) to highly unfavorable (M = 84). For each viscosity ratio, the capillary-number was varied across a wide range. The experiments show that when M is much larger than unity, the flow patterns are quite complex with a wide range of finger length scales. Overall, for a given M > 1, the instabilities associated with these immiscible displacements are more benign than their miscible counterparts. Specifically, unlike the miscible setting, immiscible instabilities are rarely dominated by of a few large fingers that bypass the resident fluid. We note, however, that the local wetting phase saturation in the flooded regions can be persistently large, indicating significant microscopic bypassing. The standard Darcy model for multiphase flow cannot fully capture these observations. Thus, a better understanding of the fluid-flow physics at the pore scale is needed in order to describe the long-time evolution of unstable immiscible two-phase flow in porous media. For that purpose, we have been studying the applicability of the Lattice-Boltzmann method (LBM) for modeling unstable immiscible two-phase drainage displacements. Our analysis indicates that existing Lattice-Boltzmann models fall well short of accurately describing the solid-fluid-fluid contacts, or resolving the fluid-fluid interfaces in complex pore structures and networks. We have also been developing numerical methods of fluid flow at the pore scale. Specifically, a projection step is introduced into the formulation of the pressure equation associated with the Navier-Stokes momentum balance. This is obtained using a mass weighted continuity equation that ensures a conservative velocity field. The jump conditions of pressure and the normal viscous stresses and the continuity of the interfacial stresses are enforced at fluid-fluid interfaces. Solid boundaries are treated using the immersed boundary method. Recently, we have been studying the applicability of various techniques, including level-set methods with the latest contact-angle models, for propagating the (drainage) interfaces through the pore network.

Porous Rock with Fluid: Impact of Heterogeneity and Scale on Relations between Rock Properties

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The objective of this work is to understand the scale dependence of relations between rock's porosity and permeability; porosity and electrical conductivity; porosity and elastic moduli; as well as cross-property relations among the said rock properties.

This work is needed because the up-to-date knowledge of the subject is mostly based on physical lab and field data or abstract mathematical derivations. Massive numerical experiments on realistic pore structures promise to quantitatively expand and qualitatively enhance this knowledge.

The scope of work is to:

- Compile and image-process a significant number (20 to 30) of digital samples of natural rock, including carbonate and tight gas sandstone.
- Conduct massive numerical experiments (fluid flow, electrical current flow, and elastic deformation) on these digital samples and their subsamples. These volumes will be used as-is and will be numerically altered to change the pore-space geometry (e.g., expand or shrink the pores) in a spatially heterogeneous fashion.
- Create a massive numerical database.
- Analyze the results of these numerical experiments to understand whether and how the obtained relations among porosity, permeability, conductivity, and elastic properties comprise trends. Validate these trends by experimental (physical) trends and theoretical rock physics models.
- Combine the properties and trends thus obtained in a larger volume and simulate processes in such volumes to understand whether and how such trends persist at a macro-scale. Specifically, for fluid flow, we will use a standard Darcy-flow simulator (rather than LBM) to calculate the permeability of a composite to understand relations between the effective permeability thus obtained and the mean porosity. For the elastic properties, we will use analytical bounds for both isotropic and anisotropic situations. For the electrical properties, we will use the same FEM code as for the mm-scale tests because the conduction process is the same (unlike fluid flow).

Structural Heterogeneities and Paleo Fluid Flow in An Analog Sandstone Reservoir

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The primary objectives are to understand the circumstances and physical processes by which a complex suite of brittle structures can evolve throughout a long geological time span in a sandstone reservoir or aquifer, and how the resulting fabric of the structural heterogeneities can act to affect the fluid flow. These objectives are relevant to the management of ground water, hydrocarbons, and the movement and safe storage of CO_2 and nuclear waste produced by fossil-fuel combustion and nuclear reactors, respectively.

Deformation bands of shear and compactive types, and faults with their associated fractures, have a broad range of size and distribution patterns and hydraulic properties, which greatly complicate the challenges faced by geoscientists working on the problems mentioned above related to energy and the global environment. The effects of these structural heterogeneities on reservoir-scale fluid flow (both actual and potential) can be assessed directly using outcrop-based studies combining field work, petrographic analysis, permeability measurements, fluid flow modeling, and geomechanical modeling, along with detailed analysis of the diagenetic alteration patterns that resulted from paleo- fluid flow. The Aztec Sandstone at the Valley of Fire State Park, Nevada, offers exceptional exposures of fractures, deformation bands, and faults at scales ranging from centimeters to kilometers in an exceptional natural analog to sandstone aquifers and reservoirs worldwide.

A current task of this project is to map and analyze the geometric, spatial, and temporal relationships between the compaction bands at high-angle to bedding and those at low-angle or parallel to bedding. This is providing a better data set on the distribution of these structures and their compartmentalization, and their relationship to the depositional architecture of the Aztec Sandstone. This data set along with the existing information on joints and small faults are also being used for 3D flow simulation. A second task is developing a 2D numerical model for the mechanical behavior of non-planar faults in order to understand the distribution of slip, stick, and opening along them, and the influence of fault geometry on consequent stress perturbations and off-fault damage. A third task is developing a computer code to evaluate Eshelby's solutions for ellipsoidal inclusions and heterogeneities, and applying this to understand the growth of compaction and shear deformation bands.

It is expected that the research outlined here will help geoscientists and engineers meet present and future challenges by providing a solid foundation, based on detailed geological mapping and geomechanical modeling, to illuminate how a complex suite of brittle structures can form and evolve to affect fluid flow in a typical sandstone aquifer/reservoir from the grain scale to the aquifer and reservoir scales.

Structural Basis for Stabilization and Transformation Behavior of Amorphous Calcium Carbonate

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The main goals of the research are to determine short- and medium-range structure in different forms of doped and undoped amorphous calcium carbonate (ACC) and to establish the role of structure in stabilization of ACC and in the mechanism and kinetics of its transformation to crystalline forms. ACC is known to form as a transient precursor to formation of crystalline calcium carbonates phases, including calcite and aragonite. The primary factors that control their stability and transformation pathway are additives, such as magnesium, phosphate, and organic macromolecules. However, an understanding of the detailed interactions of such additives is hindered by a lack of knowledge of the structure in the ACC phase. This research program combines molecular-scale techniques—synchrotron total X-ray scattering, X-ray absorption spectroscopy, NMR (1H, 13C, 25Mg, 31P), and reverse Monte Carlo refinement—to establish a structure model for hydrated amorphous calcium carbonate (ACC), including samples containing additives that influence its stability and crystallization kinetics. Short- and medium-range order in ACC and the function of additives provide the basis for stabilization and crystallization, and therefore influence formation of calcium carbonate for both biologic and inorganic pathways. A particular focus of the research is evaluation of the effect of inorganic (Mg, PO_4) and organic (amino and organic acids) additives that modify reactivity. In-situ study of transformation will identify intermediate phases and operative mechanisms. This work takes advantage of synchrotron user facilities to provide novel structural information. Results of the research will provide a structural and mechanistic basis for understanding calcium carbonate mineralization via an amorphous precursor pathway.

Reactivity of Iron-Bearing Minerals and CO_2 Sequestration: A Multi-Disciplinary Experimental Approach

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The primary goal of this research program has been to understand the chemistry that results when supercritical CO_2 with H_2S and/or SO_2 in deep saline formations contacts 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. Toward this end in-situ vibrational spectroscopy and batch reaction studies have been carried out under conditions that closely mirror those that will be present in the environment. An area of focus in the research has been to learn how the presence of H_2S in the CO_2 injectate affects the reaction of CO_2 with iron bearing minerals to form, for example, immobile mineral phases such as $FeCO_3$ (siderite). We have experimentally observed that the exposure of a series of iron oxides to supercritical CO_2 with small amounts of H_2S results in the formation of siderite and pyrite. The type and amount of product, however, is a strong function of the concentration of H_2S, reaction temperature, and solution pH. Overall, the research continues to provide insight into chemistry during sequestration that can potentially increase the long-term storage of CO_2. The techniques being used to characterize the chemistry and products are in-situ infrared spectroscopy and ex-situ techniques that include electron microscopy, Mössbauer spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy.

Time-Lapse Seismic Monitoring and Performance Assessment of CO_2 Sequestration in Hydrocarbon Reservoirs

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Funding:	$221,000

Carbon dioxide sequestration remains a compelling research topic as a potential approach for mitigating the effects of greenhouse gases on global warming. While CO_2 can be sequestered in oceanic or terrestrial biomass, one of the most mature and promising technologies is sequestration in geologic formations, especially in known hydrocarbon reservoirs. However, challenges in the design and implementation of sequestration projects remain, especially over long time scales. For the past several years, we have continued to develop methods for improved monitoring and performance assessment of carbon dioxide sequestration in geologic formations. A critical feature of our work has been fast streamline-based flow simulation of CO_2 injection combined with modeling of wave propagation for time-lapse seismic monitoring of CO_2 fronts in the reservoir, including compositional and geochemical effects. In this proposed work, we plan to incorporate geomechanical effects and their influence on the storage of CO_2. Specifically, we will develop mechanistic models to examine the changes in permeability resulting from variations in in-situ stress fields caused by CO_2 injection. We will investigate the potential for leakage of CO_2 through high resolution transport modeling across faults and fractures using streamlines. The tracing of streamlines across faults poses special challenges because of the complex juxtaposition, non-neighbor connections, and the velocity discontinuities that can arise at the fault faces. Geomechanical processes also alter the seismic time-lapse response. Our work will therefore focus on fully integrating fluid flow and seismic data for monitoring injected CO_2 fronts by developing robust methods for reservoir characterization, coupled fluid flow modeling, including geomechanically induced stress effects and associated permeability and seismic velocity changes. 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. Effective field applications also require careful, quantitative measures of uncertainty for which we propose an efficient Bayesian framework for data integration using reversible jump multistage Markov Chain Monte Carlo (MCMC) methods with hierarchical reparameterization of prior models. Finally, using field data from a CO_2 injection enhanced oil recovery project, we plan to develop a systematic workflow for the detection and location of CO_2 movement using fluid flow and seismic data.

Geochemistry of Interfaces: From Surfaces to Interlayers to Clusters

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OBJECTIVES

The objectives of this research are to develop an approach for predicting the types of metal surface complexes that form on mineral surfaces by focusing on the role of metal-anion complexes, and to incorporate these surface complexes into thermodynamic surface complexation models to predict adsorption behavior.

PROJECT DESCRIPTION

We combine the use of several techniques including bulk adsorption experiments, X-ray absorption, infra-red, and vibrational sum frequency spectroscopies (XAS, IR, VSGS), and molecular modeling to investigate ion-pairing in solution and at mineral surfaces. XAS provides data on how the metal binds to the surface (e.g., monodentate, bidentate), IR provides data on ion-pairing in aqueous solution, and VSGS provides data on the impact of adsorbed metal-anion pairs on water structure at the mineral surface. Molecular modeling is used to guide spectroscopic data interpretation by providing information on water structure around ions in solution and the structure of metal-anion complexes in aqueous solution. In addition, molecular modeling is used to provide insight into water structure at mineral surfaces, the surface sites involved in ion adsorption, and the distribution of ion pairs between aqueous solution and the mineral surface. Our studies have focused on systems involving alkaline earth metal and heavy metal cations. The anions we have selected for study include chloride, nitrate, perchlorate, sulfate and selenite. Ion adsorption and the potential formation of ternary complexes on silica (quartz, amorphous silica), alumina (corundum and gibbsite), and ferric iron (goethite) oxides are under investigation.

RESULTS

The Katz group's focus of this fiscal year included finalizing the work on temperature effects of alkaline earth metal adsorption onto gibbsite, and completion of the study for selecting surface site density with the application of charge-distribution multisite complexation (CD-MUSIC) model on various adsorption systems.

For the temperature effect study, we completed the surface complexation modeling efforts to support our macroscopic sorption data and the Criscenti group's molecular dynamics simulations to prove that divalent mercury ion adsorption occurs through both inner- and outer-sphere surface complexation depending on the temperature and the ionic radii of the metal ion. Increased reaction temperature enhanced metal ion adsorption for the three alkaline earth metals whereas it decreased the impact of ionic strength on Sr^{2+} and Mg^{2+} adsorption. It was observed from both macroscopic and molecular approaches that the tendency to form inner-sphere complexes on gibbsite decreased in the order: $Ba^{2+} > Sr^{2+} > Mg^{2+}$, and that the common assumption that alkaline earth metal ions form outer-sphere complexes appears to be dependent on ionic radius and temperature. These results highlight the importance of considering temperature when selecting inner versus outer sphere complexes for surface complexation modeling.

Surface site density has a significant role in determining the adsorption capacity of ions in a selected system. Several approaches for estimating surface site density had been evaluated by our group for the past few years of this project. We concluded that morphology and crystallographic data provides the most reasonable tool for estimating surface site density, and the CD-MUSIC model provides the most realistic description of adsorption for complex systems. We successfully predicted Pb(II)/Cd(II), Pb(II)/Selenite and Cd(II)/Selenite bi-solute adsorption on goethite with CD-MUSIC. It was determined that the model best describes bi-solute sorption/competition behavior by utilizing reactions sites from three goethite crystal faces (101, 001, and 210) with ternary complexation reactions.

The CD-MUSIC modeling approach was also applied to a tri-solute system including Hg(II)/Cl/carbonate adsorption to goethite and to gibbsite. For goethite, the theoretical analysis of crystallographic data provides surface site densities for each type of surface type group (singly (=FeOH), doubly (=Fe_2OH), and the triply coordinated surface group (=Fe_3OH)) with different proton affinities at each crystal face. The modeling studies utilized a binuclear Hg(II) surface species involving two singly coordinated oxygens as the predominant surface complex in the absence of Cl and at pH values below 8. At higher pH and in the absence of chloride, ternary Hg(II)-carbonate species dominate. In the presence of Cl, ternary surface complexes with Cl become significant and competition with carbonate and aqueous Hg-Cl species inhibit adsorption. For Hg(II) adsorption onto gibbsite, the 1-pK CD-MUSIC approach was adapted with the dominate edge(100) face as the reactive sites. The ternary Hg-Cl surface species were found to be non-reactive species in the gibbsite-water system, while the ternary surface species, =AlOHgOH1/2- was dominant in the presence of Cl. The model was verified with another Hg(II) adsorption data set by incorporating carbonate binding (=AlOCOO) to describe the decreasing capacity of Hg(II) with increasing pH. The results of this work suggest that the CD-MUSIC model is capable of predicting metal ion adsorption in complex systems and that estimation of the surface site density using crystallography, morphology and titration congruence is a valid approach.

Predicting Fracture Porosity Evolution In Sandstone

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Funding:	$300,000

OBJECTIVES

Our goal is to understand how fracture growth and diagenetic alteration interact to create and destroy fracture porosity and how this interaction affects fracture patterns. We are testing the hypothesis that records of fracture opening can be recovered from fractures formed in the subsurface and that along with fluid-inclusion data these records can help recover the duration and rates at which fractures open and rock properties change. This information can also be used to understand how entire fracture networks evolve. We are testing linked diagenetic and geomechanical models that incorporate these processes.

PROJECT DESCRIPTION

Our observations and modeling show that important mechanical and chemical feedback govern several important aspects of fracture patterning and that fracture growth patterns, timing, and opening rate can be recovered from structural diagenetic data. We use SEM-based cathodolumiescence imaging, fluid-inclusion and other geochemical data, field studies, a diagenetic model that incorporates mechanics, and a diagenetically sensitive geomechanical model to investigate how diagenesis affects development of fracture aperture, length, and spatial arrangement.

We are extending a theory of cementation in fractures that predicts fracture porosity evolution as a function of temperature, surface area, and opening history. We take advantage of automated image collection systems and protocols, fluid inclusion microthermometry, and sandstone petrography to rigorously test predictions. We also track rock property evolution in the context of burial history. We investigate how diagenesis affects fracture growth by conducting numerical experiments that incorporate diagenesis, using both our geomechanical model (a newly developed hybrid numerical code) and other modeling approaches. The geomechanical model predicts patterns, rates, and durations of fracture opening. Numerical experiments are helping us formulate hypotheses about how feedbacks work, including processes that generate fracture size distributions and clustering patterns. We test fracture growth hypotheses against natural examples from outcrop and core using high resolution fracture opening histories and fluid-inclusion data keyed to opening increments, which allows rigorous comparison with our diagenetic models. We also seek to understand causes of heterogeneous sealing of large, static fractures by carbonate cement, a widespread phenomenon that seals some large fractures.

RESULTS

Competition between fracture nucleation and growth, fracture opening rate, and cement precipitation governs overall fracture porosity, the pattern of interconnected fracture pore space, and probably the size scaling and spatial arrangement of fractures. Together these interactions influence how fractures govern fluid flow in the subsurface. A readily measured parameter in fracture populations is the opening displacement; hence this is a good attribute to use for constraining fracture mechanics model results. We used a fracture mechanics model to examine the feedback between these aperture propping mechanisms and fracture network growth. Power laws result from diagenesis active during fracture propagation. Ongoing work is making the linked fracture mechanics model truly three-dimensional and fully linked to the diagenetic model.

Opening-mode fractures in Piceance Basin sandstones display evidence of multi-step opening by the crack-seal mechanism from SEM-CL imaging of synkinematic quartz bridge cements. These cements are spatially discontinuous within individual fractures, with significant porosity preserved. These fractures have power-law aperture-size distributions. Scanline data from 12 samples indicate that as fractures widen, the power law slope decreases and approaches a value near -0.5, observed in populations with the largest fractures. This uniform power law exponent could provide a useful tool for fracture intensity prediction using small datasets of fracture size. Work underway uses fluid inclusion trapping temperature measurements linked to burial history to document the sequence of fracture nucleation and growth giving rise to size scaling fracture patterns. Results are being compared to simulations using the fully coupled mechanics-diagenesis model and various other rule-based models.

Fluid inclusion analyses of fracture cements were extended along an east-west transect in the southern Piceance basin to assess regional trends in fracture timing and in fracture opening rates. Timing of fracture opening is determined through correlation of fluid inclusion trapping temperatures with burial models constrained by stratigraphic and vitrinite data. This correlation indicates that fracture opening occurred consistently between ~42 Ma and ~10 Ma in the southern Piceance basin. Based on pore fluid pressure estimates obtained from fluid inclusion compositional analyses, we infer that fracture opening is driven by gas generation in adjacent coal layers at the time of maximum burial. To test our fracture scaling and timing results in a different depositional and structural setting, we performed field work in outcrops sandstones in the western Alberta basin. Initial results indicate good correspondence in fracture style, frequency, and diagenetic attributes between outcrop and core from producing intervals. Access to core from this basin will allow us to test all aspects of our characterization and prediction approaches.

Website: http://www.jsg.utexas.edu/sdi/index.html

Fault-Related CO_2 Degassing, Geothermics, and Fluid Flow in Southern California Basins: Physiochemical Evidence and Modeling

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OBJECTIVES

This is a collaborative study to quantify basinal fluid flow, submarine gas migration and diagenetic effects within deforming faults in a transpressional setting that is seismically active. The field application emphasis is on faulted basins in southern California.

PROJECT DESCRIPTION

We have mainly targeted active faults and young (Tertiary) petroleum fields in southern California for study. Faults include the Refugio Fault in the Transverse Ranges, the Ellwood Fault in the Santa Barbara Channel, and the Newport-Inglewood Fault Zone in the Los Angeles Basin. Subsurface core and tubing scale samples, outcrop samples, well logs, reservoir properties, pore pressures, fluid compositions, and published structural-seismic sections are being studied to characterize the tectonic/diagenetic history and geochemical signatures in carbonate that characterize rapid 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.

RESULTS

We have developed new computational models to study the various coupled processes affecting multiphase fluid migration, including effects of permeability, capillarity, and saturation that affect hydrocarbon mobility within fault systems and to search the possible hydrogeologic conditions that enable the natural sequestration of prolific hydrocarbon reservoirs in actively deforming young basins such as the Santa Barbara and Los Angeles basins. Subsurface data provide important constraints for model geometry and parameter testing, and provide critical insight on how large-scale faults and aquifer networks influence the distribution and liquid- and gas-phase hydrocarbon migration. For example, pore pressure changes at a methane seepage site on the seafloor have been carefully analyzed to estimate large-scale fault permeability, which helps to constrain basin-scale natural gas migration models for the Santa Barbara Basin. We have developed a new 2-D multiphase numerical model, and successfully modeled large-scale fluid flow for intensely faulted profiles of the Los Angeles Basin. Our simulations suggest 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 during post-Miocene time. Fault permeability, capillarity forces between fluids, juxtaposition of aquifers-aquitards, source-rock saturation, and rate of generation control the efficiency of natural carbon sequestration in sedimentary basins. We expect that this research will also contribute to an understanding of the subsurface behavior of injected anthropogenic greenhouse gases. Future modeling will focus on enhancing the stratigraphic detail and include effects of poroelasticity.

Impact of Micro- to Meso-Scale Fractures on Sealing Behavior of Argillaceous Caprocks on Carbon Sequestration

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Funding:	$200,000

Our goal is to quantify and image the nature of rock fractures in exposed analog systems that reflect the dynamic, coupled, multiphase fluid flow, reactive transport, and deformation processes that affect the transmissivity of fractures in argillaceous mudstones. We focus on mudstones since they are the most common reservoir caprocks for hydrocarbons and CO_2 storage. We achieve these objectives with a combination of field and laboratory studies. In this report, we discuss progress made in field and laboratory studies performed in the first year of the project. We focus on factors that control the embedment and development of fracture systems in otherwise high matrix seal capacity (high entry-pressure) caprocks/mudstones, characteristics of those fracture systems, and dynamic factors that degrade or improve sealing quality over the time scales of tens to hundreds of years and longer.

RESULTS

We have completed the field-based study of fracture systems within and at the transition from reservoirs to seals at four sites in southeastern Utah, and we are in the process of examining five others. In addition, we examined several faults that breach several hundred meters of caprock and have evidence for fluid-rock interactions along its entire length. Key results to date include the following:

(1) Basic elastic moduli within the cap rock can be estimated with field-based and wellbore-based methods, and reveal variations of 50-100% over scales of tens of meters to km. At the outcrop scale, these variations are manifested as discrete fractures in highly indurated interbedded horizons and diffuse fractures in the mudstones. Variability of caprock strength is significant over the scale of a field.

(2) Early fractures are reoccupied by several stages of carbonate-charged fluids, creating preferential pathways from reservoir into overlying seals. Lateral migration occurs within the caprocks, and in places, upward migration occurred far from the initial entry point of the system.

(3) Large faults that cut an entire mudstone sequence exhibit a wide range of structures and evidence for fluid-rock interactions. Faults that at one level appear to have been effective barriers to flow clearly were charged with mineralizing fluids at high structural levels.

(4) Analyses of several sites reveal that a fault type previously thought to be a barrier to lateral fluid migration may in fact be an effective flow pathway upward along the fault, perhaps by the development of fingers of fluid that access narrow fractures that form along previously slipped surfaces.

(5) New experimental data at low pressures show that gas-phase CO_2 will rapidly change ambient water pH, significantly dissolve calcite cements, and lead to fracture-flow and disintegration of reservoir and seal lithologies.

Dissolution Rates and Sorption/Catalytic Reactivity of Nanominerals and Nanomineral Aggregates

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Funding:	$156,000

The objectives of this project are (1) to investigate the effect of particle size, morphology and aggregation state on the kinetics of reductive dissolution of nanoparticulate hematite, (2) to determine size, morphology and reactive sites of nanohematite and their aggregations, (3) to determine catalytic reactivity of nanohematite by studying aqueous Mn(II) oxidation, and (4) to investigate the structure and reactivity of iron sulfides.

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 hematite with ascorbic acid has been investigated. The dissolution of hematite nanoparticles was shown to occur in two stages: initial and steady state. The surface area normalized initial rate of reductive dissolution in the case of the 7 nm hematite was about two times greater versus the 31 nm hematite. High-resolution TEM (HRTEM) of individual crystals and aggregates revealed contrasting differences in the 7 nm and 31 nm hematite; the former being free of defects and the latter displaying nanoscale steps on the surface and internal defects within the crystal. The 7 nm hematite particles were found to dissolve uniformly from the edge of the crystal with corresponding changes in the aggregation state. In contrast, the dissolution of the 31 nm hematite was found to initiate from the steps, defects, or sharp edges of the crystals. The steady state rates of dissolution for the two populations were measured to be considerably slower than their initial rates, and very similar.

Advanced TEM imaging of the 31 nm hematite, including high-resolution tomographic analysis, was used to further study the complex nature of these particles at nanometer and sub-nanometer levels. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of these nanohematites identified nanochannels within the rhombohedra that serve as an active site for dissolution. The presence of these channels suggests that large molar volume shrinkage during the crystallization of the poorly crystalline nanoparticulate precursor (ferrihydrite) generates the nanochannels in the hematite nanocrystals. The competitive kinetics between crystallization and aggregation of ferrihydrite nanoparticles are likely to play a key role in determining the morphology and the type of reactive sites (nanochannels or stacking faults) of the resulting crystals of hematite. These findings are of fundamental importance in controlling the particle size, crystal morphology and the generation of defects in nanoparticles formed from an amorphous precursor. This also continues to emphasize exact details concerning the importance of surface roughness, defects, crystal morphology, and aggregation state on the nature of the reactivity of nanoparticles.

The reactivity of nanoparticles was also tested by comparing the rates of Mn(II) oxidation catalyzed by the two size populations of our nanoparticulate hematite. Surface-area normalized rate constants again suggest differences in reactivity of hematite among the two populations. The end product of Mn(II) oxidation, a higher valent manganese oxide identified as the mineral ramsdellite (MnO_2) having a unique nanosized, fiber-like morphology, has been identified and characterized by employing a suite of analytical techniques including HRTEM, electron energy loss spectroscopy (EELS) mapping, nanometer-resolved selected area electron diffraction (SAED), and high-resolution scanning electron microscopy (SEM). Mössbauer analysis did not reveal any phase transformation within the nanoparticulate hematite following Mn(II) oxidation. These findings suggest that the formation of Mn-oxides can be influenced by the bulk mineralogical and geochemical composition of the surrounding environment, as well as by the interfacial solute–solid nanochemistry of the solid-phase oxidant.

Finally, the dissimilatory metal-reducing bacteria (DMRB) Shewanella putrefaciens strain CN32 was used to synthesize biogenic and nanometer-sized mackinawite. The biogenic mackinawite was found to be extremely reactive on exposure to air by converting to lepidocrocite. SEM analysis revealed rosette-shaped aggregates of the biogenic mackinawite. Near future research plans include further characterization of this mackinawite by TEM, HRTEM, BET surface area analysis and Mössbauer spectroscopy. Reactivity of the biogenic mineral will be tested by its propensity to reduce redox active metals such as uranium and chromium. This study signifies the relevance of low-temperature interfacial geochemistry in the formation of environmentally pertinent biogenic nanominerals.

Investigation of the Physical Basis for Biomineralization

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Funding:	$259,000

This project is directed at determining principles that govern interactions of simple protein analogs and key inorganic impurities with carbonate minerals and the resulting structures, polymorphs and signatures that form. Our investigations are focused on four novel areas of research: (1) initial stages of nucleation and onset of polymorph selection, (2) matrix mineral relationships, (3) mineralization pathways, and (4) the dependence of isotopic signatures on mineralization pathways and biomolecular constituents. Over the last year, we have published or have in press, a number of new publications that uncover biomolecule controls on carbonate growth and show their thermodynamic versus kinetic controls on mineralization. We have also made new insights into the controls of organic templates on

$CaCO_3$ nucleation, $CaCO_3$ nucleation pathways, the role of Mg and supersaturation in redirecting $CaCO_3$ formation towards dolomitic compositions, the kink dynamics that determine step growth on calcite, and microscopic controls on trace element and isotopic fractionation. To our knowledge, these results are novel to the literature.

In new work, the last 12 months have also been an exciting time of discovery while resolving obstacles for measuring rates of carbonate mineral nucleation and for working with ACC. Having solved these problems, a number of additional manuscripts are now in various stages of preparation that demonstrate the kinetics of carbonate nucleation onto a suite of biosubstrates. These include functionalized SAMS (surface assembled monolayers) and highly characterized polysaccharides.

Thanks to support from DOE, the findings from this work are an important step toward establishing a revised mechanistic and quantitative understanding of controls on carbonate mineralization in organic-rich biological and sedimentary environments.

Interface Induced Carbonate Mineralization: A Fundamental Geochemical Process Relevant to Carbon Sequestration

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Carbonate mineralization has been at the forefront of surfacial geochemistry for the past two decades and is attracting more attention recently due to the concerns of possible feedbacks of high atmospheric CO_2 to global climate as well as the need for carbon sequestration. Our investigations in the current funding period focused on the following two aspects of carbonate formation: (1) template effect on the crystallization of $Ca\text{-}CO_3$ and (2) solvent effect on the precipitation of $Mg\text{-}Ca\text{-}CO_3$. The motivation to study template effect stems from the need to understand how silicates affect the nucleation and growth of Ca-Mg-carbonates in geological carbon storage media. In this area, we investigated calcite crystallization on mineral of mica and pyroxene to determine the orientation relations between calcite and the substrates.

Our results show that both biotite and muscovite have strong controlling effects on calcite nucleation and orientations of the calcite crystals. The primary orientation relationship between the growing calcite crystals and mica substrate are: calcite (001) ~//mica (001) and calcite (010) ~//mica (010). Our analysis indicates that calcite crystals initially nucleate from the Ca^{2+} layers and occupy the original K^+ sites on the mica surfaces, followed by the attachment of CO_3^{2-} groups on the calcium monolayer to form the first unit cell of calcite. The geometry of this Ca^{2+} layer, which matches the calcite structure, could be the control factor on calcite a-axis direction. The slight difference (with overall area mismatch of +1%.) can be accommodated through distortion of the first calcite layer. Pseudo-hexagonal symmetry on biotite and muscovite (001) surfaces leads to the observed (001) twinning in calcite. Mica substrate can enhance Mg incorporation into calcite. As much as 19% $MgCO_3$ can incorporate into the calcite lattice using a solution with Mg/Ca ratio of 5.

Based on the results from both natural and synthesized samples, pyroxene like diopside ($CaMgSi2O_6$) can also enhance epitaxial growth of calcite with preferred orientations. Calcite a-axis is about parallel to diopside c-axis. The observed large interface area between diopside and synthesized calcite indicate that the exposed Ca^{2+} and Mg^{2+} ions on surfaces with pseudo-hexagonal arrangements may serve as heterogeneous nucleation sites and therefore lower the nucleation energy barrier.

We have studied the effect of dissolved hydrogen sulfide and polysaccharides on incorporating Mg into Ca-Mg-carbonates and the formation of dolomite at room temperature in aqueous solutions. The adsorbed molecules served as catalysts that can lower the dehydration energy barrier of surface Mg^{2+}-water complexes dramatically, and 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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This project is developing and applying new techniques for in-situ stable isotope analysis. Procedures have been developed for the analysis of isotope ratios for O, C, Mg, Si, Li, S, and Fe using a CAMECA IMS-1280 ion microprobe. We are investigating applications of the new analytical technology to CO_2 sequestration, paleoclimate, fossil fuel reservoirs, and groundwater and hydrothermal systems. Significant advances have been made in the analysis and interpretation of stable isotope compositions, zonation, and exchange.

We are studying the genesis of diagenetic cements and degradation of porosity in clastic sedimentary rocks. Thin syntaxial quartz overgrowths and detrital quartz grains have been investigated from different geological environments and analyzed for d18O and d30Si with unprecedented small spot size (1-15 µm), and high accuracy and precision (0.1-0.2‰) (Valley and Kita 2009; Kita et al. 2009). These studies have examined mineral zonation and exchange kinetics to distinguish the effects of pedogenesis and vadose zone precipitation versus burial and diagenesis or low temperature hydrothermal precipitation. The analysis of sample volumes 106 to 109 times smaller than previously possible by laser fluorination allows us to contour d18O across individual quartz overgrowths. Mineral zonation patterns provide new insight into mechanisms and timing of water/rock interaction, and migration of fluids through sandstone aquifers. We have applied experience gained by microanalysis of syntaxial quartz overgrowths in the Saint Peter sandstone to quartz cements in the Mount Simon sandstone and overlying Eau Claire shale. New results show that deeply buried Mount Simon quartz overgrowths are zoned by up to 8‰/50µm in d18O recording growth during burial and heating (Pollington et al. 2011). We have found similar zoned cements in the Eau Claire Formation (Hyodo et al. in prep); Ness Formation, North Sea; and Wilcox Formation, Texas (Harwood et al. 2012). Analysis of silicon isotope ratios in quartz overgrowths is underway to evaluate the importance of groundwater silcretes during early cementation and if silica is derived from pressure solution versus clay reactions in shales in deeper samples. DOE-sponsored Regional Partnerships, MGSC and MRCSP, have drilled an injection well for a mega-ton CO_2 sequestration experiment in the 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.

Phase Transitions and Crystal Orientations in Marine Invertebrate Skeletons: Key Insights into Biomineral Formation Mechanisms and Function

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Biominerals, including bones, teeth, mollusk shells, and many others, are formed under direct control of living organisms. We do state-of-the-art microscopy and spectroscopy experiments to elucidate key biomineralization mechanisms that have long puzzled the geochemistry community. Specifically, we 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.

Fluid Chemistry, Surface Chemistry and Fracture Mechanics: An Investigation of the Connection at the Nanoscale

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Funding: $116,000

We seek to address several problems of critical importance to understanding geochemical processes that occur during the geologic sequestration of CO_2. Specifically, we want to understand the geochemical behavior of the CO_2-aqueous fluid-rock system under the near-equilibrium conditions that will be obtained over the bulk of the lifetime of the sequestration process. Geochemical models effectively treat dissolution/growth as a crystallographically isotropic process whereby a solid surface is modeled using one type of surface site, yet we know that surfaces are significantly more complex than their model counterparts. Recent macro-scale and micro-scale studies in our lab have focused on (1) understanding how the surface reactivity of a mineral varies as a function of crystallographic surface orientation and (2) describing the morphological relaxation that occurs on a mineral's surface in response to a change in fluid composition. Our approach to addressing these questions is to apply a combination of microscopic and macroscopic experimental techniques that permit us to study process details at the specific mineral-fluid interfaces and then to "scale-up" to integrate those processes over all surfaces. Specifically, in-situ experiments using our unique Hydrothermal AFM (HAFM) and batch reactors were conducted on carbonate mineral specimens to characterize the processes of topographic relaxation, crystal face specific dissolution rates, and crystal morphology evolution on a nanometer to micrometer distance scale.

Corresponding macro-scale experiments were conducted using flow-through reactors. Utilizing elementary step speed information from in-situ hydrothermal atomic force microscopy (HAFM) investigations of calcite dissolution as a function of solution saturation state and temperature as input to a surface topographic decay model, we hypothesized that the evolution of the dissolution rate in our macro-scale experiments would occur on timescales from 5-100 minutes. These experiments, carried out in near-equilibrium fluids, revealed several important and unexpected characteristics of the calcite-water interface. First, the observed dissolution rate in our macro-scale experiments evolved on a timescale of 100 hours, nearly two orders of magnitude longer than predicted. The initial model therefore was examined in light of new data from crystal-face specific studies showing that dissolution of calcite in near equilibrium fluids leads to the development of low-reactivity facets, surface features that were not incorporated into the original topographic decay model. Second, HAFM images demonstrated that the predominant elementary step orientation depends on saturation state, suggesting that most previous observations of calcite step edges which were made in far from equilibrium solutions, do not simply extrapolate to near equilibrium conditions. Third, to address questions raised by our initial investigation above, we further investigated the influence of solute impurity concentration, using magnesium as a proxy. In solutions as dilute as 0.001 molal Mg, the solution saturation state acted as a “switch” for magnesium inhibition, yielding highly non-linear response of step edge motion to fluid chemistry. Neither the evolution of surface reactivity, as expressed in the surface morphology, nor the non-linear behavior of dissolution in impurity-laden solutions is captured in current geochemical models used for reactive transport modeling. The kinetics of near-equilibrium calcite dissolution examined in this work provide accurate experimental data under likely CO_2 sequestration conditions, and thus are crucial to the development of robust geochemical models that predict mineralogical evolution and the long-term performance of geologic containment scenarios.

DOE National Laboratories

Mineral-Fluid Interactions: Synchrotron Radiation Studies at the APS

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Funding:	$600,000

This activity seeks to develop a fundamental molecular-scale understanding of mineral-water interface processes that control the geochemical transport and cycling of elements in Earth’s near-surface environment. Processes of interest include adsorption/desorption, growth/dissolution, and oxidation/reduction reactions. These reactions 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 which 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 help bridge the gap between the actual processes and the idealized conceptual models that are used to interpret field-scale observations, will further define kinetics and reaction mechanisms at the atomic scale in key mineral-fluid systems, and will constrain the continued development of theory pertinent to mineral-fluid interface processes. We will address these gaps in our understanding through (1) experimental observations of elementary mineral-water interface processes in well-defined systems and (2) direct comparison of measurements to computational results. Our emphasis is 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. 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 necessary for the development of robust predictive capabilities associated with the release and geological disposal of energy-related byproducts.

Density-Driven Brine Convection: A Process for Accelerating CO_2 Dissolution and Enhancing Security of Geologic Storage

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Funding:	$175,000

Carbon dioxide (CO_2) injected into a permeable rock stratum will be stored via four major mechanisms: (1) bulk containment of the mobile supercritical phase CO_2, (2) small-scale trapping by capillary forces, (3) dissolution into the local brine, and (4) chemical reactions with aqueous species and host rock resulting in mineral precipitation. The security and permanence of CO_2 storage increases along this pathway from containment to mineralization. After injection into the subsurface, the less-dense free-phase CO_2 will tend to rise to the top of the permeable formation and will accumulate beneath a confining layer (cap rock) as a result of buoyancy. Beneath the confining layer, the CO_2 will spread out, governed by capillary, buoyant, and viscous forces, forming a relatively horizontal layer at some distance from the injection location. CO_2 in contact with local fluids will begin to dissolve into the fluids. The dissolution of CO_2 into the brine will result in increasing the brine density. Brine with increased density located over less dense brine will result in a fluid dynamics instability such that the heavier brine containing CO_2 will tend to flow downward. This will cause lighter brine without dissolved CO_2 to move upward, contacting the CO_2 plume, dissolving more CO_2, and then convecting downward. This dissolution-induced density-driven convection is a desirable process because it can significantly enhance the CO_2 dissolution rates, thereby increasing storage security. In previous years, we performed laboratory visualization studies in homogeneous transparent cells and quantitative CO_2 absorption tests in homogeneous sands at elevated pressure to investigate this phenomenon. Our numerical modeling of the tests was performed with results comparing favorably with experimental results. Because the natural environment is typically heterogeneous and anisotropic, in FY 2011, we performed a number of visualization tests examining the effects of anisotropy and heterogeneity on density-driven brine convection using similar techniques as for the homogeneous systems. Using the results of the visualization tests, we have performed a suite of quantitative experiments to examine the effects of anisotropy on density-driven brine convection. Comparison and analysis of these tests is ongoing.

Detection and Monitoring of Fluids, Faults and Coupled Processes in the Earth's Crust - unified proposal

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Funding:	$1,245,000

Fluid injected into the Earth's subsurface for a host of industrial applications (CO_2 sequestration, geothermal energy generation, ground water cleanup, enhanced oil recovery) causes the porous rocks to deform and often induces fracture and/or slip along faults. The overall goal of this research is to understand in a quantitative way the coupling between flow and deformation and damage so that measurements of the deformation and damage along with changes in geophysical rock properties may be used to determine where the fluid is flowing and what processes the flow is provoking. The specific objectives of this interdisciplinary project 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 properties of the subsurface change during fluid injection and through induced damage, 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 what the injected fluid is doing in the subsurface.

The project began October 1, 2010. In the first year, the seven key senior personnel all performed research toward achieving the above goals. Steve Pride worked on understanding the seismic properties of granular media (that are highly sensitive to fluid injection/extraction); Jim Berryman worked on the mitigation of seismicity induced by fluid flow with applications to geothermal energy and CO_2 sequestration, as well as on the seismic properties of granular media; Don Vasco worked on forward and inverse modeling procedures for monitoring fluid injection at CO_2 sequestration sites using surface deformation data; Greg Newman worked on joint seismic and EM coupled inversion methods; Lane Johnson worked on theoretical slip models on faults and how they couple to fluid pressure; Seiji Nakagawa worked on a range of new laboratory (experimental) set ups that allow seismic properties to be measured as a function of effective pressure and fluid saturation, including the response of both single fractures and granular media; and Valeri Korneev worked on the physical modeling of fluid waves in fractures. Considerable collaboration necessarily occurred between these overlapping efforts.

Integrated Isotope Studies of Geochemical Processes

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Funding: $825,000

OBJECTIVE

The primary objectives are to better understand (1) the molecular to micro-scale processes that control isotopic fractionation during mineral precipitation and transport in fluid phases and (2) the field scale behavior of isotopic ratios in fluid-rock systems and its relation to large scale hydro-geochemical processes. Objective 1 is aimed at developing molecular scale models for mineral formation at both high and low temperatures, using isotopic and trace element fractionation effects as a monitor of molecular fluxes at the mineral surface. An additional objective is to develop models for isotopic fractionation during diffusion in liquids. Objective 2 involves development of new geochronological techniques as well as methods for characterizing transport in larger scale geologic systems using isotopes of solid radiogenic elements (Sr, Nd, Pb, Ca, U, etc.), light stable isotopes (O, C, H, Li, N, S, Ca, Fe, etc.), and noble gases (He, Ne, Ar, Kr, Xe).

PROJECT DESCRIPTION

Molecular to micro-scale processes are addressed with experiments and measurements on natural systems focused on Ca and Mg isotopic fractionation 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 studies of isotopic effects due to fracture flow and inhomogeneous permeability in fluid-rock systems.

RESULTS

(1) U-Th-He: We continued study of U–Th/4He ages on olivine phenocrysts from late Quaternary basalts. The approach employs abrasion to remove implanted 4He from U-rich groundmass and an extraction system that allows U, Th, and He concentrations and isotopic compositions to be measured on the same sample. Initial results on submarine Hawaiian tholeiitic basalts have so far been difficult to interpret, but complications may be due to mass spectrometer issues, related to the very low He contents of the examined olivines. Recent improvements are leading to the first age data using this system.

(2) Ca isotope probe of mineral precipitation: The mechanisms and rates at which dissolved ions are transferred to and from mineral surfaces as crystals grow from aqueous solution are poorly known but important for interpreting mineral chemistry and isotopic composition. Ca and Mg isotopes can provide unique information about the mineral-fluid interface. Results from studies of diagenetic systems, which evolve over millions of years, indicate that at equilibrium, there is no Ca isotopic fractionation during

precipitation of calcite. However, Ca isotopic effects are different in clay-bearing sediments; the presence of abundant clay and/or organic material appears to decrease the already slow dissolution rates of calcite to effectively nil. This effect may explain the improved preservation of fossil carbonate in clay-bearing or marly limestones.

(3) Theory of isotopic fractionation during mineral precipitation: A macroscopic kinetic-thermodynamic model has been developed that relates isotopic and trace element fractionation to precipitation rate. This model so far explains well the observations of Ca isotope fractionation when calcite is precipitated under surface reaction controlled conditions, and also explains the partitioning of Sr/Ca and Mn/Ca. Model results suggest that as equilibrium is approached, molecular exchange rates between mineral and solution decreases. This theory has been extended to an ion-by-ion calcite growth model, which results in explicit relationships between Ca and CO_3 ionic exchange rates, their dependence on solution oversaturation as well as on Ca:CO_3 ratio in solution, and kinetic and energy parameters for binding of ions to the calcite surface.

(4) U-series alpha-recoil as a nanoscale probe of natural systems: ($^{234}U/^{238}U$) of fine-grained sediments shows systematic effects suggesting that alpha-recoil associated with the decay of ^{238}U is primarily responsible for ^{234}U depletions in minerals. Because the rate of ^{234}U loss reflects the scale of recoil, which is 30-50 nm, and the shape and surface properties of mineral grains, the U-series characteristics of minerals constitutes a nanoscale probe of mineral surface structure. Models for quantifying the alpha-recoil loss fraction based on theoretical estimates of recoil range, mineral grain geometry, surface area constraints, and chemical methods have been developed.

(5) Field scale Ca isotope effects in hydrothermal systems: A survey of the Long Valley hydrothermal system is continuing for the isotopes of water, Sr, Ca, and noble gases and the concentrations of major cations, anions, and total CO_2. Correlated variations among total CO_2, noble gases, and the concentration of Ca suggest progressive fluid degassing, driving calcite precipitation as the fluid flows across the caldera and generating an increase in fluid d44Ca. Studies have also been done on epidote from fossil basaltic hydrothermal systems. Hydrothermal calcite and epidote show evidence of Ca isotope fractionation, which is most likely due to kinetic effects during precipitation that are analogous to and similar in magnitude to those that affect calcite precipitating at 25°C.

(6) Phase partitioning tracers: Modeling has shown that precisely measured details of a chromatographic separation profile for a suite of phase-partitioning tracers with different gas-water solubility can provide important information regarding gas/liquid transport, the extent of gas-water interaction, and an integrated gas/H_2O volume ratio and can place constraints on the geometry of gas-liquid interaction. Quantitative assessment of tracer return data is limited by a lack of data regarding the solubility partitioning of the tracers in water-CO_2 systems at the relevant P, T, and xi conditions. Preliminary water-CO_2 solubility experiments for noble gases and SF6 have been conducted under the appropriate P, T, and xi conditions encountered in deep aquifer CO_2 sequestration that indicate a significant increase in noble gas solubility in water in the water-CO_2 system, ranging from a factor of ~3 for Ne to a factor of ~10 for Xe.

(7) Collaborative studies: We collaborate with other BES investigators on isotopic fractionation due to diffusion in aqueous fluids and silicate liquids, and in modeling isotopic effects using numerical reactive transport codes. The diffusion studies have the dual objective of characterizing the isotopic effects for application to natural geochemical processes and using them to understand the chemical structure of fluids and melts. The modeling studies relate isotopic effects to models of mineral reaction kinetics, in order to allow isotopic measurements to be used as monitors of chemical reactions in nature.

Inv. of the Physical Basis for Biomineralization III

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Funding:	$200,000

OBJECTIVES

This project is directed at determining principles that govern interactions of simple protein analogs and key inorganic impurities with carbonate minerals and the resulting structures, polymorphs, and signatures that form. A long-term goal is to establish the physical basis for biomineralization in natural and engineered Earth systems.

APPROACH

For this work, we are pursuing four novel areas of research: (1) the initial stages of nucleation and the development of polymorphs, (2) matrix-mineral relationships, (3) mineralization pathways, and (4) the dependence of isotopic signatures on mineralization pathways and biomolecular constituents. Nucleation studies include classical MD calculations of desolvation; ion association and clustering; in situ AFM measurements of nucleation rates on model organic matrices, including organothiol SAMs and polysaccharides; and in situ transmission electron microscopy investigations of nucleus formation and phase evolution. Growth studies include ICP mass spec analysis of calcium isotopes in sea urchin spicules and in calcite derived through both classical terrace-ledge-kink growth and ACC-to-calcite transformation with and without acidic polypeptides, as well as nano-SIMS studies of impurity distributions across the ACC-calcite nanoparticle composite that comprises individual spicules.

RESULTS

In the past year, we have developed new insights into biomolecular controls on carbonate growth and the relative roles of thermodynamic and kinetic factors in mineralization, the controls of organic templates on the pathways and kinetics of $CaCO_3$ nucleation, the role of Mg and supersaturation in redirecting $CaCO_3$ formation towards dolomitic compositions, the fundamental kink dynamics of steps on calcite surfaces, and microscopic controls on trace element and isotopic fractionation during both ACC and calcite formation. Many of these new findings have either been published, are in press, or are in manuscripts in preparation.

Mineral Surface Geochemistry

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Funding: $800,000

OBJECTIVES

The overall objective of this project is to provide a deeper understanding of the geochemistry of mineral surfaces in subsurface environments through the application of nanoscale and laboratory-scale experimental probes along with modeling approaches.

PROJECT DESCRIPTION

Specific topics to be investigated in the current project include (1) thin water film hydraulic properties and solution chemistry, including solute diffusion and electrical double layer structure; (2) mechanisms of adsorption and precipitation reactions on mineral nanoparticles; and (3) topographic relaxation induced by thin water films on mineral surfaces during dissolution processes.

RESULTS

(1) We developed a model to predict adsorbed water film thickness over a broad range of matric potential, solution ionic strength, and interfacial electrostatic potential representative of soils and unsaturated rock fractures. Our calculations indicate that adsorbed film thicknesses in the range of nanometers to tens of nanometers occur in many water-unsaturated soil and rock environments. A newly-designed film equilibration chamber has been tested, yielding film thickness measurements qualitatively consistent with our calculations.

(2) We measured the adsorption of Zn on birnessite (layer type MnO_2) under conditions of varying pH, Zn concentration, background electrolyte, and time of Zn addition. Birnessite has a high affinity for Zn and extended X-ray absorption fine structure (EXAFS) spectra, analyzed by principal component analysis, linear combination fitting, and structural fitting show that Zn forms a triple-corner-sharing complex at vacancy sites, with a mixture of one (Zn-IV-TCS) or three (Zn-VI-TCS) oxygens from water, irrespective of pH and surface loading. We find that the Zn-IV-TCS species is favored at low loadings. At pH values of 6-8, the amount of Zn-IV-TCS plateaus at high loadings, whereas the amount of Zn-VI-TCS increases with increasing loading. We used a multiple-technique, scanning electron microscope (SEM) and X-ray approach to correlate the reactive surface area of a rock where carbonate precipitation reactions occur with the connected pore structure. The pore structure was measured in small volumes and at resolution < 1 µm by FIB-SEM, as well as in larger volumes and at lower resolution by synchrotron-based X-ray µ-tomography. The spatial distributions of the silicate and carbonate mineral phases in contact with the pores were determined with SEM-BSE and µ-XRF coupled with an image-thresholding technique, as well as SEM-EDX and µ-XRD. These data were then combined with larger-scale reactive transport experiments, augmented by pore- and continuum-scale modeling, to interpret the effects of pore connectivity on geochemical reactivity.

(3) We used both solution analyses and surface topographic techniques to study mineral dissolution as a function of solution composition and crystallographic orientation for calcite and diopside. Procedures were developed to study both bulk mineral and face-specific reactivity. Our results clearly show that reactivity is strongly related to crystallographic orientation (calcite and diopside), saturation state (calcite and diopside), and, for diopside, silica activity due to the formation of silica-rich surface alteration layers.

The Center for Nanogeoscience

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Funding:	$950,000

The Nanogeoscience Center had significant results on a number of supported projects.

Electron hopping rates in iron oxides: In previous BES-funded research, we developed a method to study interfacial electron transfer reactions relevant to environmental redox processes and applied this to the reductive dissolution of iron oxide, an important component of the global iron redox cycle. In FY 2011, we used this approach to perform the first direct measurements of the electron hopping rates in three ferric iron oxide phases. The hopping rates range from 0.2 - 0.35 ns^{-1}, and represent a fundamental limit on the reductive reaction rates of these phases.

Pyrite (001) interface structure and lead surface complexation: Pyrite, FeS_2, is the most common sulfide mineral, and it can strongly impact surface water quality through oxidative reaction or by the adsorption of aqueous ions. In previous BES-funded research, we performed a surface diffraction study of the hydrated pyrite (001) surface; we have now complemented this with X-ray diffraction and extended X-ray absorption near edge structure (EXAFS) spectroscopy of lead cations absorbed to this surface. The data obtained in these studies will aid the structure solution of the hydrated (001) surface and additionally reveal the Pb^{2+} sorption geometry.

Corundum r-plane (1-102) and a-plane (1-100) interface structure as a function of pH: By using sum-frequency spectroscopic methods, we have been able to characterize the surface structure, surface hydroxyl types and orientations, and water structure as a function of pH on these planes. It was shown that the acid-base properties of the interfaces are directly related to the types of hydroxyls, which in turn are controlled by the specific surface terminations. On the r-plane, chains of hydrogen bonds extend along the glide plane trace directions, and these persist despite variation in solution pH. Points of zero charge and water polar orientations were also obtained.

Iron oxyhydroxide nanoparticle formation and nucleation: We have used classical MD to study early stages of iron nanoparticle formation in ferric iron aqueous solutions containing different degrees of hydroxylation. Early processes involve formation of chains of edge-sharing octahedral units, which eventually coalesce into more dense clusters. Later development shows the beginnings of 3D structure at the nm scale. The concentration of hydroxls present strongly affects cluster formation. From the experimental side, we have used quick EXAFS, optical spectroscopy, and SAXS to collect information about early precipitation in aqueous solutions. The process is highly sensitive to the hydroxide/metal ratio and the availability of base during the neutralization. Clear transformations in the type and order of clusters are evident, especially when sulfate is also present as in acid-mine-drainage formation. Complementary Cryo-TEM work has also been done to investigate nucleation and growth from these solutions, and provide direct structure and morphological information on nucleus and early growth sequences.

Uranyl sorption and reduction on magnetite surfaces: Combined in-situ surface EXAFS and XANES, AFM-studies, XPS spectroscopy, and surface X-ray diffraction have been used to determine the speciation of uranyl sorption on magnetite (111) surfaces and the mechanism and rate of reduction into U^{4+}. Uranyl was reduced in cases where no Ca^{2+} was available in solution independent of CO_3 content but sorbed as stable Ca^{2+}-carbonate complexes when both CO_3 and Ca^{2+} were in solution. Reduced U formed nm-sized nanoparticles associated with surface defects, and a mechanism for e-transfer from the interior structure of the magnetite was developed to explain the reaction kinetics.

Evaluating the Ability and Limitations of Geophysical Electric Resistance Tomography to Track Moving Multiphase Fluids in Porous Media

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Funding:	$200,000

The primary objective of the proposed research is to explore how the nature of multi-phase flows in porous media influences the electrical resistivity distribution of the fluid-filled porosity in the context of electrical resistance tomography (ERT) imaging. We have conducted a series of novel bench-scale porous flow combining electric resistance tomography (ERT) imaging with optical visualization of fluid flows in a porous medium. This comparison approach allows us to relate the development of a flow in a porous medium to high resolution ERT images of the changing electrical resistivity distribution in the porous medium created by that flow. This work has bearing on any attempt to image flows in a porous or subsurface regime. We developed a 2D thin-cell system in which a sand layer is confined between two vertical optically transparent glass plates separated by one centimeter. Stainless steel ERT pin electrodes (22 with centimeter separations) penetrate each of the vertical sides of the plastic spacer separating the glass plates. This particular cell has a vertical-to-horizontal aspect ratio of about 2:1. The cell is sufficiently thin that the quartz sand readily transmits light from a lamp situated behind the cell to a ccd camera mounted in front. Each of the ERT electrodes are connected to a channel of a data acquisition system that allows a schedule of 4-wire current measurements to be made that are required to compile the ERT imaging data set. Following construction of two identical cells at LLNL, they were set up in the imaging lab at UC Irvine, where all experiments have been performed to date. In FY 2011, we performed a series of experiments that allowed comparison between optical flow and tracer concentration measurements and simultaneous ERT flow and concentration observations. This work is very timely because of its connection to the ongoing LLNL ERT imaging effort in Cranfield, MS, which is part of a DOE NETL sponsored CO_2 injection and carbon sequestration study. The LLNL ERT system, which is the world’s deepest deployment of ERT, has recently produced images of CO_2 saturation; subsequent analysis of these images can greatly benefit from understanding how ERT images of injected fluids in porous media relate to the actual characteristics of the injected CO_2 plume (volume, saturation, distribution of injectate, etc.). Using the test section described above, one experiment involved injecting CO_2 into the cell at the base and allowing it to rise until trapped beneath the overlying lower permeability layer. Detailed analyses of volume and concentration were performed on both sets of data. It was generally found that the ERT significantly under-predicted the injected volume of CO_2. This result coupled with improvements in how we relate resistivity to CO_2 saturation (Archie's Law) will have a direct effect on the role of imaging of CO_2 injections in the subsurface.

Geochemical Imaging with Nano/SIMS

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Funding:	$100,000

The objective of the project is to develop the operating procedures and fundamental parameters required for the routine application of the NanoSIMS, the latest development in elemental and isotopic microanalysis, to geochemical problems by addressing issues that require its analytical sensitivity and spatial resolution. Current efforts are focused on the partitioning of moderately siderophile elements between core-forming metallic liquids and silicate melts, utilizing experiments performed in piston cylinder and mulit-anvil apparatus and in the laser heated diamond anvil cell. The pattern of siderophile (iron-loving) element abundance in the silicate portion of the Earth is a consequence of metal separation during core formation. The apparent excess of nickel and cobalt in mantle-derived rocks has been attributed to metal-silicate equilibration in a deep terrestrial magma ocean. Based on the extrapolation of phase equilibria and metal-silicate partitioning results obtained at lower P and T, previous estimates of the pressure and temperature of equilibration are all greater than 25 GPa and 3000 K (the high limit of the available dataset) for single-stage core formation. Using the laser-heated diamond anvil cell (LH-DAC), we have extended this pressure and temperature range to 75 GPa and 4400 K, exceeding the liquidus temperatures for both metal and silicate and, therefore, more directly applicable to estimation of the depth of the magma ocean. The metal-silicate partition coefficients, D_M^(met-sil), for nickel and cobalt decrease with increasing pressure and reach the values required to yield present mantle concentrations at ~50 GPa. At these conditions, silicon (X%) and oxygen (X%) concentrations in the metallic liquid are sufficient to resolve the seismically constrained core density deficit. Above 60 GPa, the partition coefficients become too low, resulting in an overabundance of Ni and Co in the silicate mantle. These data provide an upper bound for the depth at which the Earth's core may have formed and reconcile both the geophysical (density) and geochemical (excess siderophile) issues.

Kinetic Isotope Fractionation III

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Funding:	$50,000

The primary objective of this project 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. Research activities in the past year focused on two areas: (1) Li isotopic analysis of an experimental charge quenched from basaltic liquid and (2) revision and publication of a manuscript on an experimental evaporation study of chondrule-like liquids. A thermal diffusion experiment was previously completed to investigate Li isotopic fractionation along a thermal gradient in a basalt liquid. In this experiment, basaltic starting material was doped with Li (500 ppm) and the charge was run in a piston cylinder assembly that was intentionally displaced from the hot spot to generate an approximately 200°C temperature gradient across the experimental charge. The Li isotopic profile of the experimental charge was previously measured using the modified ims-3f ion probe at LLNL. However, due to non-optimal instrument operating conditions at that time, the results were ambiguous. The sample was re-analyzed earlier this year with the ims-3f. The data confirm a slight gradient in Li isotopic compositions, of ca. 6 parts per thousand amu, corresponding to the thermal gradient in the experimental charge. Following the analysis by ion microprobe, the experimental charge was sectioned along the thermal gradient, and the resulting pieces were subjected to bulk analysis of Li isotopic composition by MC-ICP-MS. The resulting analyses had smaller uncertainties than the ion probe measurements, and confirmed the existence of a thermal diffusion profile in the charge. Other research activities this year resulted in the publication of a paper [“Laboratory experiments bearing on the origin and evolution of olivine-rich chondrules,” by F. M. Richter, R. A. Mendybaev, J. N. Christensen, D. Ebel, and A. Gaffney, in *Meteoritics and Planetary Science* (2011), v. 46, p. 1152-1178]. This work uses the results of an experimental evaporation study of chondrule-like liquids to conclude that olivine-rich Type IA and Type IIA chondrules from Semarkona evolved in a partially closed system where the residence time of the surrounding gas was sufficiently long for it to become saturated in the evaporating species (K) and for there to have been effectively isotopic equilibrium between the gas and the melt.

Quantification of Mineral Precipitation Kinetics Using Solution Chemistry and NMR Spectroscopy

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$225,000

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 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. In FY 2011, we investigated surface mediated precipitation of Al in the presence of amorphous silica, and the interactions between surfaces and paramagnetic cations. Our study on the Al/SiO_2 system indicates that despite a range of thermodynamic driving forces (temperature, pH, and Al concentration) favoring formation of $Al^{[6]}$ containing phases (i.e., gibbsite or kaolinite), $Al^{[4]}$ phases dominate the NMR spectra of samples where Al is reacted with amorphous silica. By combining ^{27}Al multiple quantum magic angle spinning (MQ/MAS) NMR, $^{27}Al\{^1H\}$ rotational echo double resonance (REDOR) NMR and empirical modeling of the ^{27}Al NMR chemical shifts for the $Al^{[4]}$ species, we identify these phases as metastable, hydrated aluminum-tectosilicate phases. In a subset of samples, we also identify additional $Al^{[6]}$ species, which we assign to allophane-like phase which are precursors to kaolinite formation. Importantly, we do not observe species that we would identify as surface sorbed Al despite conditions favoring their formation. It would seem that even at reasonably low Al concentrations, the formation of metastable aluminosilicate phases is the dominant reactions process. In studying the interactions between the paramagnetic cations Ni^{2+} and Cu^{2+} and the amorphous silica surface, we have seen that solid state NMR techniques provide a sensitive probe of the surface structure. We analyzed the intensity differences in solid-state $^{29}Si\{^1H\}$ cross-polarization (CP)/MAS NMR spectra for sorbed samples versus control samples with chemometrics analyses to probe these interactions at low surface loadings (<3%) and show that these cations preferentially sorb at deprotonated silanol surface sites ($>SiO^-$). Additionally, we show that the presence of admixed paramagnetic solids ($Ni(OH)_2$) cannot produce the same affects seen for the sorption samples. These results indicate that the techniques developed may be a sensitive probe for surface mediated processes over bulk precipitation.

230th-238u Disequilibrium Measurements

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$250,000

This project is about measuring, modeling, and understanding isotopic distributions over a range of spatial and temporal scales. It highlights the development of new tools, techniques, and facilities for mass spectrometry. The primary analytical tools we employ are uranium-series geochemistry, bulk and micro sampling techniques, and mass spectrometry. The emphasis is on processes that modify and alter the physical and chemical state of earth materials.

Currently we are working to (1) continue development of micro analysis methods for actinide studies, (2) use femtosecond laser ablation to measure U-series transport in U-rich fractures, (3) investigate near surface transport of anthropogenic and natural components in soil cores, and (4) demonstrate in situ methods for uranium-series geochronology of corals.

This work will contribute to our understanding of the geochemistry of mineral-water interactions and assessment of radioactive waste repositories, along with other hydrologic and geochemical processes. These techniques will also have applications to human evolution, plate tectonics, forensics, and climate change. Finally, the new methods, new understanding, and newly trained researchers that result from this work can contribute to interests, such as environmental monitoring and threat reduction, of other agencies.

A New Probe for Understanding Rock Elasticity - Time of Flight Modulation

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$250,000

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 (DAET) 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 application to monitoring thermal induced mechanical damage in nuclear repositories, application to probing borehole integrity, as well as geotechnical applications including 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. Our work utilizes the new probe for Earth materials, including materials exposed to supercritical CO_2 as well as Earth materials subjected to pressure, temperature, and humidity. The research initiates development of a model that provides predictive capability relating elastic nonlinear response to mechanical damage intensity. This second, ambitious goal will not be fully realized in the duration of the 3 years of our work but will, at the very least, provide basic scientific constraints and define initial aspects of a new model.

Summer of Applied Geophysical Experience (SAGE)

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Funding:	$35,000

Objectives of SAGE 2011 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 make contributions to a number of national security areas, such as 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 2011 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. A 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.

Mineral Transformations in Supercritical CO_2-Dominated Fluids: Impact on Caprock Integrity

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Funding:	$70,000

This project lead by PNNL aims to understand the physical and chemical processes taking place at mineral surfaces in contact with carbon dioxide (CO_2) + water mixtures. The project addresses fundamental science questions relevant to the long-term caprock integrity of carbon sequestration sites. The ORNL-led part of the project concerns the study of the pristine and reacted minerals (e.g., olivine, muscovite) and the properties of sorption phase formed at the mineral grain surfaces. Neutron scattering experiments (SANS) carried out at the neutron sources in Oak Ridge and NIST Gaithersburg will measure the surface area and fractality of different minerals found in cap rock formations (i.e., phyllosilicates and orthosilicates) in pristine and reacted states. The pristine and reacted minerals will be provided from our collaborators at PNNL. The second subtask studies the sorption from mixtures of CO_2 and water (D_2O) to pristine and reacted mineral surfaces. The goal of this SANS study is to measure the density and composition as well as the volume (thickness) of the sorption phase for different conditions of temperature and fluid mixture composition. The combined analysis of neutron scattering and sorption analysis data will feed into new models for quantitative description of the sorption behavior of binary mixtures at mineral surfaces. The ORNL effort will be synergistically linked to the overall project, leading to a novel understanding of complex geo-fluids in natural environments.

Structure and Dynamics of Earth Materials, Interfaces and Reactions

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Students:	3 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$1,850,000

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 will 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 will utilize 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.

Molecular Mechanisms of Interfacial Reactivity in Near Surface and Extreme Geochemical Environments

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Students:	3 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,250,000

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 dynamics of mineral interfacial reactions and the changes induced in mineral surface chemistry by electron conduction/transfer reactions; (2) determining the impact of oxidation/reduction reactions on the transformations of multivalent metal solutes/adsorbates at mineral surfaces, with a special emphasis on determining reaction intermediates; (3) developing a mechanistic understanding of solvation, hydrolysis, and mineral/acid base chemistry, including reactions at high temperature and pressure and in supercritical fluids; and (4) developing new experimental and 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.

SISGR: The Role of Interfacial Processes on Mineral Transformations in Wet Supercritical Carbon Dioxide

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Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $632,000

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.

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. Further studies using new HIM imaging coupled with FIB/SEM sectioning through the reacted mineral surface has revealed the nature of the secondary mineral nucleation and growth centers. 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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Funding:	$750,000

The mineral-water interface provides the critical setting for many geochemical processes in the environment. The surface properties of the mineral substrate 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 seen significant advances in recent years, there remains a significant gap in our knowledge of structure, reactivity, dynamics, and molecular-level mechanisms of mineral surfaces and interfaces (including the confined interlayers of clay minerals) as well as nanoscale molecular clusters that are dominated by surfaces comprised of oxygen, hydroxyl, and water ligands.

This project combines theoretical, computational, synthetic, and spectroscopic tasks to examine the nature of complex geochemical interfaces. Specific tasks include the analysis of surface speciation, adsorption phenomena, surface complexation modeling, ion pairing, interlayer structures, parameterization of edge surfaces of clay minerals, and synthesis of molecular clusters as well as the structure and reactivity of their surfaces sites. Theoretical efforts emphasize the use of large-scale molecular dynamics simulations, ab initio molecular dynamics, and related density functional theory and classical methods to address structure and thermodynamics of mineral-water systems. A task to develop a second generation classical force field for large-scale simulations of interfacial phenomena in mineral-water systems is also included. A variety of experimental and spectroscopic work complements the theoretical effort. These tasks incorporate nuclear magnetic resonance, X-ray absorption, second harmonic generation, sum frequency generation, infrared and Raman vibration, small-angle X-ray scattering, and inelastic neutron scattering spectroscopies as well as more conventional characterization methods to understand the key molecular processes and help validate the modeling studies.

Pore Network Evolution and Chemo-Mechanical Coupling in Mudstones

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Funding:	$200,000

This research investigates coupled mechanical and chemical dynamics of mudstones, including five specific tasks: (1) measurements of influence of fluid chemistry on mudstone pore network evolution via permeability and electro-osmotic (semi-permeable membrane properties) effects; (2) acoustic measurements of changes in mudstone anisotropy, poro-elastic properties, and swelling/contraction associated with pore fluid chemical changes; (3) measurements of influence of elevated temperature, phase changes, and compaction/creep on mudstone permeability and membrane efficiency; (4) quantitative three-dimensional imaging of organic distribution and pore networks in mudstones; and (5) modeling mudstone geomechanics and pore network evolution. Methods involved in this research include moderate pressure and temperature flow through experiments; large sample flow-through experiments with acoustic emissions; microscopic visualization experiments with a sapphire cell; load frame and laser scanning confocal microscopy (LSCM); dual beam SEM/Focused Ion Beam (FIB) imaging of pore structures, including micropillar compression with nanoindenter; and pore scale modeling. Central questions are: Can macroscopic properties like membrane efficiency, permeability, and swelling responses be reconciled with nano- and pore-scale observations? How do microscopic changes driven by chemistry influence macroscopic mechanics? How do macroscopic swelling displacements partition at the pore scale? How are mudstone mechanical properties and anisotropy scale-dependent and influenced by fluid chemistry?

RESULTS

3D FIB/SEM work involved comparing pore topologies and pore-lining phases of connected flow pathways in mudstones, as well as modeling gas flow through connected pores in kerogen-bearing portions of mudstones. Collaboration with Navarre-Stichler and colleagues is examining application of neutron scattering to pore topology for a number of mudstone microfacies. Along with traditional mercury porosimetry, there appears to be one scaling relationship for “nanopores” residing in clay packets, another for “micropores,” and yet another for kerogen-bearing portions. The type, volume %, interconnectivity, and distribution of these pore types control single and multiphase flow properties (calculated from computational fluid dynamics modeling in micropores), mechanical response, and membrane properties. 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. Work continues on (transversely anisotropic) inversion methods for acoustic tomography of mudstones, membrane efficiency tests linked to pore network properties and pore-lining phases during creep consolidation, and Poisson-Boltzmann methods applied to water properties in micro- and nanopores. Direct 3D observation of nanopore topologies will be performed in coming months using a novel confocal TEM method.

Heavy Element Chemistry

Institutions Receiving Grants

Fundamental Chemistry of Actinide Complexes Containing An-N, An-O, and An-S Bonds

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Funding:	$125,000

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 fuel cycles. Recent studies of the reaction chemistry of An-H and An-C bonds (An = U, Th) have shown that surprising new structures and reactivity patterns are available from well-established classes of actinide complexes, some of which have been known for decades. This project will attempt to expand similarly the limits with other donor atoms and especially nitrogen.

Uranium Complexes for the C-H Activation of Hydrocarbons

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Funding:	$166,000

The objective of this research project is to generate electrophilic uranium centers for the activation and functionalization of small and inert molecules. In addition, this research provides training of graduate students as the next generation of actinide scientists.

The reactivity of uranium dibenzyl complexes supported by a 1,1'-ferrocenylene diamide with aromatic N-heterocycles was investigated. The relevance of aromatic heterocycles to natural products and pharmaceuticals has prompted a concerted research effort toward their synthesis and functionalization. Aromatic heterocycles also appear as unwanted impurities in carbon-based fuels and, recently, processes that fragment them are becoming prominent. Interestingly, d0fn metal-carbon bonds show diverse reactivity toward aromatic heterocycles; functionalization as well as ring opening have been reported. Specific to actinide chemistry, since aromatic N-heterocycles are used in separation columns for actinide processing, understanding the interactions between the actinides and materials/molecules is also critical to a number of applications within the DOE complex. Expertise in the production, processing, purification, characterization, analysis, and disposal of actinide elements is essential to the U.S. national security. In this way, our studies add to the intense field of research focused on inert molecule activation and functionalization reactions, and to actinide chemistry relevant to radioactive waste processing.

Exploring the Redox and Oxo Substitution Chemistry of the Uranyl Ion: Implications for Separations and Environmental Remediation

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Funding: $120,000

The uranyl ion (UO_2^{2+}), a major component of nuclear waste, does not easily undergo chemical change. Attracted by this challenge, we have developed the 'Reductive Silylation' methodology for modifying this extremely stable fragment. We began this study by evaluating ligand environments that are best suited to stabilize the reduced form of uranyl (UO_2^{+}), and we developed the β-ketoiminate (R-acnac) framework for this purpose. This ligand class creates a bulky, substitutionally inert ligand environment that prevents further coordination of Lewis bases to the uranyl equatorial plane. Using the acnac ligand system, we discovered several examples of uranyl functionalization, including 'Reductive Silylation', wherein the uranyl moiety is both reduced by one electron and silylated, in an efficient one-pot procedure. For example, reaction of $UO_2(^t\text{Bu-acnac})_2$ with excess Me_3SiI, in the presence of Ph_3P, results in reductive silylation of the uranyl moiety to afford the U(V) bis-silyloxide complex, $[Ph_3PI][U(OSiMe_3)_2I_4]$ (**1**). Like uranyl, the O-U-O angle in **1** is 180°; however its U-O bond lengths (1.99 Å) are significantly longer than the U-O bonds in uranyl. In essence, complex **1** is no longer a uranyl complex, but a U(V) alkoxide. The formation of complex **1** is also remarkable in that Me_3SiI is acting as a reducing agent. Surprisingly, addition of Lewis bases, such as 2,2'-bipyridine, to **1** induces a second one-electron reduction and formation of a U(IV) bis-silyloxide complex, $U(OSiMe_3)_2I_2(\text{bipy})_2$ (**2**). Normally the 6+ uranyl ion is challenging to reduce to U(V) or U(IV); however, our results reveal that a rich redox chemistry can be accessed by silylation of the uranyl moiety.

Interestingly, addition of silanes, such as $HSiPh_3$, to $UO_2(\text{R-acnac})_2$ under the same experimental conditions results in no reaction. This was surprising, considering that R_3SiH was anticipated to be a substantially better reducing agent than Me_3SiI. Given this, we turned our attention to the $B(C_6F_5)_3$-mediated hydrosilylation methodology. $B(C_6F_5)_3$-mediated hydrosilylation is known for a variety of organic substrates including ketones, aldehydes, imines, alkenes, and even CO_2. Gratifyingly, silylation of a uranyl oxo ligand, concomitant with reduction to U(V), can be achieved via addition of $HSiPh_3$ and $B(C_6F_5)_3$ to $UO_2(\text{Ar-acnac})_2$, resulting in the formation of $U(OSiPh_3)(OB\{C_6F_5\}_3)(\text{Ar-acnac})_2$ (**3**) and dihydrogen. During the reaction we suspect that a transient borane-silane intermediate, $[B(C_6F_5)_3\text{-}HSiPh_3]$, promotes a nucleophilic attack of the silyl cation by the uranyl oxo ligand, resulting in O-Si bond formation.

Currently, only a few substrates can effect 'Reductive Silylation', but these initial studies hint that further examples are waiting to be discovered. In addition, these findings demonstrate the importance of functionalizing the uranyl oxo ligands to access the 4+ state, an observation that may have implications for the bio-remediation of uranyl in the environment or the remediation of uranyl in spent nuclear fuel.

Spectroscopic and Theoretical Studies of Prototypical Actinide Compounds

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Funding:	$130,000

The role of the 5f electrons in actinide bond formation is one of the central issues of actinide chemistry. This is a subtle question that can be investigated using a combination of strategic experimental measurements and state-of-the-art theoretical calculations. The primary objective of the ongoing program at Emory University is to obtain high-resolution spectroscopic data for prototypical actinide molecules in the gas phase. There is a critical need for such data as the results obtained from condensed phase measurements are complicated by solvent-solute or lattice interactions. For the current stage of theoretical method development, the presence of these perturbations in the test data set can often obscure the relationship between measured and observed properties.

The proposed studies are focused on the characterization of the ground and low-lying electronic states of prototypical actinide compounds. These are the states that determine both the physical and chemical properties of the molecules, and they are also the most amenable for detailed theoretical investigations.

Experiments carried out to date show that photoionization techniques are particularly well suited for studies of the low-lying electronic state structures of cations. In the proposed program we intend to extend this approach to studies of the low energy states of neutral molecules through the application of negative ion photodetachment spectroscopy. A new instrument will be constructed for these measurements. Photodetachment spectra will be recorded using the slow electron velocity map imaging technique.

The range of species to be examined in this program include Th-, U-, UO, UH, UF, UO_2, CUO, Th_2 and U_2. Measurements for the atomic anions will provide the first determinations of the electron binding energies. All of the molecular species are chosen on the basis of the specific electronic structure insights that each system has the potential to provide. Analyses of the data will be carried out in collaboration with theoreticians who are working at the forefront of relativistic quantum chemistry development.

In terms of education, the broader impact of this program is that it provides excellent training for graduate students and research experience opportunities for undergraduate students. The experiments involve advanced instrumentation, and the interpretation of the results requires the application of high-level theoretical methods.

Control of Hydrothermal UO_2N+ Systems: A Solution Phase Approach to New Solid State Materials

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Funding: $100,000

Research efforts have been proceeding in two primary focus areas: (1) in-situ ligand synthesis (ISLS) reactions as a means to producing novel uranyl hybrid materials and (2) exploring the charge transfer vibronic transitions in uranyl tetrachloride materials. The ISLS approach to materials synthesis is a relatively recent development in hydrothermal chemistry in that organic species nominally intended to be 'linker' molecules in the formation of extended topologies undergo oxidation, rearrangement or cleavage under reaction conditions. This is often the only route to a given material as starting with preformed organic species (e.g., the products of the ISLS) frequently leads to different phases. Reports of these phenomena have been increasing in frequency, yet remain largely serendipitous. Our group has been focused on determining reaction mechanisms for oxalate formation, alkly halide oxidation and nitrile hydrolysis with the goal of moving from 'seredipity' to controlled and reproducible pathways. As such we have elucidated uranyl assisted ring openings in the [UO_2]2+ - PMC/PZC/PDC systems (where PMC = pyrimidine-2-carboxylic acid; PZC = pyrazine-2-carboxylic acid and PDC = pyridine-2-carboxylic acid). These results contradict many previous reports of oxalate formation via reductive coupling of CO_2. [Andrews and Cahill, *CrystEngComm*, 13(23), 7068-7078].

Turning to spectroscopic efforts, a manuscript reporting results of a low temperature spectroscopic study of charge transfer vibronic transitions has been accepted in J. Phys. Chem. A. Therein we discuss the appearance of zero phonon lines (at low temperature) that are attributed to the first group of the excited states formed by electronic excitation from the 3s ground state into the fd,f orbitals of uranyl cation.

Self-Assembled Ionophores: Continuing in New Directions

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Funding: $140,000

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, 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) design self-assembled ionophores that selectively bind ions, and (3) construct supramolecular structures that function as synthetic ion channels.

SIGNIFICANT ACHIEVEMENTS DURING 2010 – 2011

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 mechanism of ion transport and also develop more improved analogs.

We also extended our use of self-assembly to prepare compounds that transport Cl- and HCO_3- anions across bilayer membranes. Using various assays with 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). These compounds' ability to transport Cl- and HCO_3 - at micromolar concentrations, their low molecular weight and simple preparation make them valuable leads in drug development and also lead platforms for building new approaches at selective ion separations.

Eight papers were published in 2010-2011 that were supported by this DOE Grant.

Actinide Incorporation and Radiation Effects in Layered Structures

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Funding:	$100,000

From the mining of uranium to the disposal of spent nuclear fuel, the fate and transport of actinide elements in near-surface environments is of great importance in evaluating the environmental impact of the nuclear fuel cycle. Presently, there is only a limited fundamental understanding of the atomic-scale processes that will control the mobility of actinides in the environment. Because of their generally low concentrations, except for U and Th, there is considerable evidence that actinide concentrations in groundwater and soils are controlled either by co-precipitation reactions by which actinides are incorporated into the structures of other minerals (e.g., U(VI)-phases) or by sorption onto mineral surfaces, often clays. The vast majority of U(VI)-phases and clays are layered-structures. These uranyl and silicate layered-structures share many important properties that can affect the mobility of actinides in the environment. We propose a continuation of a research program, consisting of experimental, computational and analytical studies of synthetic and natural materials, that will elucidate actinide interactions with layered-structures. In addition, an important and unique feature of U(VI)-phases and sheet silicates is that their structural and chemical properties are susceptible to radiation-induced transformations caused by alpha-decay of actinides. The damage process, and subsequent annealing, has an important effect at the atomic scale, which in turn affects the fate actinides, such as Pu and Np, that have been incorporated into the structure of the U(VI) phases. Conversely, the thermodynamic stability of a phase is closely related to its susceptibility to radiation damage. The radiation response of these phases will be studied by a combination of electron beam and heavy-particle irradiations.

GOALS

(1) Develop a fundamental understanding of the interactions between actinides and layered-structures, mainly uranyl phases and sheet silicates.

(2) Evaluate the energetics of the incorporation of actinides into layered-structures.

(3) Evaluate the role of different surfaces on the energetics of sorption of actinides onto layered-structures.

(4) Determine the structural and composition controls of layered-structures on the effects of radiation damage and annealing that result from ionizing radiation.

Multiconfigurational Quantum Chemical Study of Molecules and Ions Containing Actinides and Lanthanides

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Funding:	$200,000

Bess Vlaisavljevich has worked on actinide containing systems present in the gas phase and in a solid matrix. The aim of the project is to determine the structure and vibrational frequencies of actinide containing species, which are made in the laboratory of Professor Lester Andrews, University of Virginia. In particular, we have performed CASSCF/CASPT2 and DFT calculations on the $UO_2(Ng)_4$ species, [Ng=Ne, Ar], demonstrating that the noble gas matrices can change the electronic structure of trapped molecules. We have studied the NUN, NU and NUNH species Effective bond orders based on the CASSCF orbitals were also computed.

In collaboration with the laboratory of professor Michael Duncan, at the University of Georgia, we have studied uranium and uranium dioxide carbonyl cations. These species have been produced by laser vaporization and have been studied with mass-selected ion infrared spectroscopy in the C-O stretching region. Dissociation patterns, spectra, and quantum chemical calculations established that the fully coordinated ions are $U(CO)_8^+$ and $UO_2(CO)_5^+$. Back-bonding in $U(CO)_8^+$ causes a red-shifted CO stretch, but back-donation is inefficient for $UO_2(CO)_5^+$, producing a blue-shifted CO stretch characteristic of nonclassical carbonyls.

Daniel Grant has performed quantum chemical studies on the dehydrogenation reactions $[(C_5Me_5)_2AnH_2]_2 \rightarrow [(C_5Me_5)_2AnH]_2 + H_2$ (An = U, Th). These organoactinide hydride complexes act as four electron reductants releasing hydrogen gas. The calculated structures for both reactants and products are in good agreement with the available experimental crystal structures. The dehydrogenation reaction for the U species was calculated to be near thermoneutral (~-2 kcal/mol) and substantially less endothermic than the equivalent thorium reaction by 26 kcal/mol. This study will generate a publication in collaboration with Professor W. Evans, Irvine.

We have performed a quantum chemical and classical molecular dynamics simulation study of some solutions containing chloride salts of La^{3+}, Gd^{3+}, and Er^{3+} at various concentrations (from 0.05 to 5 M), with the purpose of understanding their structure and dynamics and analyzing how the coordination varies along the lanthanide series. In the La-Cl case, nine water molecules surround the central La^{3+} cation in the first solvation shell, and chloride is present only in the second shell for all solutions but the most concentrated one (5 M). In the Gd^{3+} case, the coordination number is ~8.6 for the two lowest concentrations (0.05 and 0.1 M), and then it decreases rapidly. In the Er^{3+} case, the coordination number is 7.4 for the two lowest concentrations (0.05 and 0.1 M), and then it decreases. The counterion Cl- is not present in the first solvation shell in the La^{3+} case for most of the solutions, but it becomes progressively closer to the central cation in the Gd^{3+} and Er^{3+} cases, even at low concentrations. With the same approach we are currently studying solutions containing the Th^{4+} cation in the presence of different counterions.

We have studied several experimentally characterized complexes containing heterobimetallic bonds between f-block (uranium and thorium and several lanthanides) and other elements. Geometries in good agreement with experiment were obtained at the density functional level of theory. The CASSCF/CASPT2 method was applied to further understand the electronic structure of the Lanthanide/Actinide-metal (or metal-metalloid) bonds. Fragment calculations and energy decomposition analyses were also performed and indicate that charge transfer occurs from one supported metal fragment to the other, while the bonding itself is always dominated by ionic character.

We have tested several methods, among which the CASPT2, CCSD, and CCSD(T) levels of wave function theory and seven density functionals against experiment for predicting the ionization potentials and bond dissociation energies of actinide monoxides and dioxides with their cations. The goal is to guide future work by enabling the choice of an appropriate method when performing calculations on actinide-containing systems. We found that four density functionals, namely, MPW3LYP, B3LYP, M05, and M06, and three levels of wave function theory, namely CASPT2, CCSD, and CCSD(T), give similar mean unsigned errors for actinide–oxygen bond energies and for ionization potentials of actinide oxides and their cations.

We have several other studies in progress related to the grant. We are working on actinide containing species on which Lester Andrews is performing matrix isolation experiments, like for example, CUC, neutral and ionic species. In collaboration with Professor Gregory Girolami, University of Illinois, Danylo Zherebetskyy is studying some thorium-boron-hydride complexes like the dianion $[Th(BH_4)_6]^{2-}$ species and the monoanion $[Th(BH_4)_5]^-$, which is a linear polymer. These systems have a potential interest for chemical vapor deposition purposes.

Preorganized and Immobilized Ligands for Metal Ion Separations

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Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$145,000

This project is focused on the discovery of fundamental electronic and structural features that influence the recognition and binding of metal ions by donor group functionalized organic architectures. The primary emphasis is directed toward selection of actinide and lanthanide fission product ions as they are encountered in nuclear materials found in the DOE complex. The experimental program involves an iterative process of ligand design, ligand synthesis, metal ion coordination chemistry, structure determination and separation analysis. Those systems that reveal new, improved structure-function performance are then used to guide the continuing ligand design/synthesis activity. At the present time, the specific major efforts in the ligand design/synthesis program are directed at geometric and electronic modifications of CMPO, NOPO and NOPOPO architectures in which multiple hard and soft donor sites serve, in favorable examples, to encapsulate f-block ions. For those systems that show useful metal ion partitioning under two phase solvent extraction conditions, ligand modifications are sought that permit either attachment of the active binding site to a polymer support or inclusion of the ligand fragment in a reversible polar-nonpolar solvent system. Such systems have the potential to eliminate or at least reduce the need for organic solvents in large scale nuclear separations.

Functionalized Scaffolds as a New Approach to the Design of Ion-Selective Polymer-Supported Reagents

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Funding:	$145,000

Research is focused on the synthesis of a new polymer with phosphate ligands surrounded by groups capable of hydrogen bonding and a new polymer for the selective complexation of the silicate ion from groundwater. Activities include (1) immobilization of phosphate-modified cyclodextrin and its high affinity for the uranyl ion and (2) anion exchange and the complexation of silica.

Fundamental Chemistry of Technetium-99 Incorporated Into Metal Oxide, Phosphate and Sulfide Materials: Towards Stabilization of Low Valent Technetium

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Students:	4 Postdoctoral Fellow(s), 5 Graduate(s), 4 Undergraduate(s)
Funding:	$400,000

The isotope Tc-99 (max ß: 293.7 keV, half-life: 200,000 years) is of interest and concern for two reasons: (1) Tc-99 is a major product of U-235 fission in nuclear reactors and (2) large amounts of Tc-99, formed during early plutonium production activities, are present in the radioactive waste stored in underground tanks at Hanford and Savannah River. The physical properties of Tc-99 and its complex oxidation-reduction (redox) activity pose a problem for both closing the nuclear fuel cycle, remediation of waste tanks and remediation of soils and waters around sites.

The overall research goals of this SISGR is to elicit molecular level understanding of the chemical bonding, speciation, and redox stability of Tc-99 incorporated into inorganic materials. This information should be useful towards controlling the extensive redox chemistry of Tc-99 and towards identifying appropriately stable waste-forms for Tc-99 based on the fundamental chemistry of the element. The SISGR team is investigating Tc-99 containing materials that range in size from molecules (nanometer-sized polyoxometalates and phosphates) to sulfide, phosphate, carbonate solid-state materials.

Computational Studies of NMR Chemical Shifts in Open-Shell Actinide and Lanthanide Systems

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Funding:	$140,000

The main objective of this project is to develop and apply new theoretical methods for the computation of ligand paramagnetic NMR (pNMR) chemical shifts in lanthanide and actinide complexes with unpaired electrons using a density functional theory (DFT) framework. These methods will be also tested by computations of transition metal complexes. The project goals include developments to enable relativistic DFT computations of all required pNMR spectroscopic parameters with the NWChem quantum chemistry package (now open source), along with additional developments using the Amsterdam Density Functional (ADF) package, and analysis of the results in chemically intuitive ways. Relativistic effects are treated by means of all-electron calculations using the variationally stable two-component zeroth-order regular approximation (ZORA).

Experimentally Characterizing the Electronic Structures of f-Electron Systems Using Advanced High Resolution Fourier Transform Microwave Spectroscopie

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Funding:	$65,000

This project concerns the use of Fourier transform microwave spectroscopy to investigate the geometric and electronic structures of heavy element-containing compounds. The project was initiated, and DOE funds were used to purchase laser ablation targets of depleted uranium, neodymium, and several other heavy elements such as tin, barium and lead. Preliminary to the actinide experiments, new data has been collected on barium monosulfide and tin monochloride. The analysis of this data is almost complete and ready for publication. The uranium experiments, in which uranium will be ablated in the presence of a variety of backing gases and the ablation products characterized are ready to run.

One graduate student has been trained to use the equipment, and two undergraduates performed senior research projects directly related to the proposed work.

At the close of the first year of support the lead investigator relocated the required instrumentation from the University of North Texas to Wesleyan University. This move was successful and is finished. At present we await the re-establishment of the DOE award in order to continue this work.

Actinide Transition-Metal Chalcogenides and Pnictides

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Funding:	$70,000

The overall objective of this grant is to increase our knowledge and understanding of Th, U, and Np solid-state chemistry.

More specifically, the objectives are to synthesize new transition-metal chalcogenides and pnictides of these actinides, to characterize them structurally, to determine selected physical properties, and to develop theoretical insights into these properties. Whenever possible, only compounds that we can characterize by single-crystal methods have been studied. Physical properties measured have included optical band gaps, magnetic susceptibilities, specific heats, and transport properties. In collaboration with Prof Donald Ellis, some DFT and related calculations have been performed.

Detailed results on $UFeS_3$ and $UFeSe_3$, UCuOP and NpCuOP, Np_3S_5 and Np_3Se_5, $Tl_3Cu_4USe_6$ and $Tl_2Ag_2USe_4$, and three complex neptunium thiophosphate compounds have been published.

Our present work on U has led to a number of new compounds, many of which have new structure types. These include the $A_2UM_3Q_6$ and $A_2U_6M_4Q_{17}$ compounds where A = alkali metal, M = Pd or Pt, and Q = S or Se. Dr. Eun Sang Choi of the National High Magnetic Field Laboratory at FSU has studied the magnetic properties of these compounds and obtained some very interesting preliminary results.

Our present work on Th compounds includes the syntheses of the new ternary compounds $Rb_2Th_7Se_{15}$, Th_2GeSe_5, and $ThLn_2S_5$ (Ln = Y, Tb, Er), and the new quaternary compounds $TlCuThSe_3$ and $TlThSb_2Se_6$. Theoretical DFT calculations of electronic structures on the compounds AnQ, AnQ_2, and AnOQ (An = Th, U, Np, Pu; Q = S, Se, Te) are being made. The calculated optical band gaps will be compared with our experimental results.

Our work on Np compounds has been stalled for more than six months owing to numerous non-scientific problems at Argonne National Laboratory.

New Synthetic Methods and Structure - Property Relationships in Neptunium, Plutonium, and Americium Borates

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Funding:	$135,000

Our overall research goals are to answer the following questions:

- What are the crystalline structures of An(III, IV, V, VI) (An = U, Np, Pu, Am, Cm) borates?
- How can unusual structural features be related to important physical properties?
- Can disproportionation of the An(V) oxidation state be used as a synthetic strategy for preparing mixed- and intermediate-valent compounds?
- How stable are these materials?

Significant achievements during 2010-2011include the following:

- We have prepared and structurally characterized more than 50 new actinide borates in oxidation states ranging from +3 to +6.
- We have prepared an entire family of uranyl borates with important nonlinear optical properties, many mixed-valent neptunium borates with unusual bonding, and several plutonium borates.
- For the first time, we have developed air-free techniques for manipulating low-oxidation states of plutonium in molten boric acid.

There are several challenges that remain. Our science objectives for 2011-2013 include the following:

- Prepare mixed-valent plutonium and americium borates, and microscale synthesis of curium borates.
- Develop calorimetric techniques for measuring the heats of formation of all of the compounds that we have prepared.

Topological Structural Relationships, Cation-Cation Interactions, and Properties of U(VI), Np(V), Th(IV) Compounds

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Funding:	$135,000

OVERALL RESEARCH GOALS

(1) 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, delineate the conditions under which such interactions are favored, and understand the impact of U(VI) cation-cation interactions on structural stability.

(3) Crystallize Th oxide nano-scale clusters (polymers), guided by small-angle X-ray scattering studies of mother solutions, and study the crystal-chemistry of Th.

Accurate Theoretical Approaches for Studying Actinides and Other Heavy Elements in Solid State

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Funding:	$135,000

The theoretical treatment of solids containing actinides or other heavy elements remains a significant challenge. Actinide f electrons can partially localize at the actinide center, can delocalize into conduction bands, and can form covalent or ionic bonds. Because multiple electrons can localize at the actinide center, actinides have multiple possible ground states distinguished by their magnetic properties. Accurately treating the various behaviors of the f electrons and the various magnetic states is not generally possible for conventional density functional methods, but does seem within the capabilities of the HSE screened hybrid developed in the PI's group.

This proposal seeks to continue the development of advanced quantum techniques capable of describing the diverse behaviors of actinide solids. Actinide solids are important elements in nuclear reactors; for example, actinide oxides are typical nuclear fuels. Actinide nitrides and carbides have prospective use as advanced nuclear fuels due to their superior refractory properties. Experimental work on these compounds is plagued by their variable composition. Theoretical investigations of the kind proposed here can help in the interpretation of DOE-sponsored experimental research on these systems and can suggest future experiments.

The Synthesis, Structures, and Chemical Properties of Macrocyclic Ligands Covalently Bonded into Layered Arrays

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Funding: $60,000

Our goal is to investigate separations based upon a new class of porous layered nanoparticles. These compounds have been found to reject or have a very low affinity for monovalent ions, low affinity for divalent ions and high selectivity for tri- and tetravalent ions. We have found that Kd(letter d supposed to be subscript) values of 105(number 5 supposed to be superscript) – 106(number 6 supposed to be superscript) are obtained for lanthanides at pH of 3-3.3 and much lower with more acidic solutions. Thus, group lanthanide separations from other ions have been effected. We are now investigating separations of lanthanides from actinides by oxidizing the actinides to higher oxidation states to obtain yl ions of charge +1 or +2. We have been able to oxidize Pu, Np, Am in this range and will carry out separations in the next two months at Los-Alamos, Carlsbad. Separation of Am iron Cm is a distinct possibility. Other separations are in the planning state.

The question to be answered is, "Why do these porous zirconium and Sn(IV) phosphonates behave in this manner?" Because they are amorphous we have to use unconventional methods of structure determination. We are initiating a program of obtaining structural information by utilizing EXAFS and atomic pair distribution functions. In addition, we have prepared similar but not identical compounds of aluminum as fine powders with a reasonable X-ray powder pattern. We are in process of solving this structure and examining the ion exchange behavior of this aluminum compound.

Synthetic Receptors and Sensors for Actinide Cations and the Pertechnetate Anion

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Funding: $165,000

This project is focused on two basic themes. The first of these involves the incorporation of the electron rich, redox active tetrathiafulvalene (TTF) subunits into known actinide complexing ligand frameworks. The goal of this effort is to create colorimetric sensors. This has led to the production and testing the TTF-huggisphyrin, a modified version of an actinide-complexing ligand originally developed by the PI's group and independently by that of Professor Jason Love. These systems are now being developed as "redox switchable" actinide receptors in conjunction with Dr. Stosh Kozimor of Los Alamos National Laboratory (LANL). Short terms are thus to scale up the synthesis of a lead system so as to permit detailed analyses of its actinide complexation chemistry at LANL. To complement this effort, a new TTF-functionalized macrocycle, a derivative of a ligand termed grandephyrin studied previously in the context of this DOE-funded research program, is being designed and synthesized. Here, again, the goal is to obtain quantities sufficient to permit detailed testing at LANL.

The second major theme being pursued under the aegis of this grant involves the study of ion pairing effects and their application to selective separations. Here we have been targeting both the sulfate anion and the cesium cation. To target sulfate, we are preparing so-called tripodal receptors. These form stable complexes with the hydrogen sulfate anion (formation constants, K, as high as 1.3 x 106 M-1 in CH3CN are observed), but display very little affinity for the nitrate anion or the halide anions. They are thus of possible interest in the context of putative tank waste treatment protocols that rely on the pre-removal of sulfate to facilitate vitrification and the production of waste forms suitable for long-term storage. In order to achieve the selective recognition and subsequent release of the cesium cation, new crown-calix[4]arene calix[4]pyrrole hybrids are being prepared. The best of these are able to extract cesium salts under conditions of liquid-liquid extraction, but then release it when contacted with aqueous solutions containing the potassium cation. This could be a model for a new recognition strategy for eventual use in the remediation of tank waste. This part of the project is being carried out in collaboration with Dr. Bruce Moyer and his group (i.e., Drs. Ben Hay, Neil Young, and, Laetitia Delmau) at the Oak Ridge National Laboratory (ORNL).

Spectroscopy, Thermochemistry, and Reactivity of Lanthanide and Actinide Molecules

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Funding:	$15,000

In this project, we are performing experiments to understand the spectroscopy, thermochemistry, and reactivity of small lanthanide and actinide species. Although some work will be pursued on the lanthanides, the focus of the project is on the more interesting actinide molecules.

Thermochemical work has been pursued using guided ion beam mass spectrometry in the Armentrout group. The reactions of thorium cation (Th+) with several atmospheric gases (N_2, O_2, CO_2, D_2O, CO) have been studied using guided ion beam tandem mass spectrometry. The reactions of Th+ with O_2 and CO_2 proceed exothermically to produce ThO+ with efficiencies compared to the Langevin-Giomousis-Stevenson (LGS) model cross sections of k/kLGS= 1.21 ± 0.24 and k/kLGS= 0.82 ± 0.16, respectively. Additionally, ThO^{2+} is formed endothermically in the reaction of Th+ with CO_2 with a reaction threshold of E0 = 6.55 ± 0.12 eV. The reaction of Th+ with D_2O is exothermic, producing ThO+ (75%) and ThOD+ (25%) with an efficiency compared to the average dipole orientation (ADO) model of k/kADO= 0.70 ± 0.14. ThD+ was also formed in this reaction with a threshold of E0 = 4.80 ± 0.38 eV. The reactions of Th+ with N_2 and CO are endothermic with thresholds of E0 = 3.07 ± 0.35 eV for the ThN+ channel, E0 = 2.69 ± 0.28 eV for the ThO+ channel and a preliminary E0 = 7.58 ± 0.18 eV for the ThC+ channel. Pairing the threshold energies with the bond dissociation energies of the respective neutral gas yields the following bond dissociation energies for the thorium compounds of D0(Th+-D) = 0.40 ± 0.38 eV, D0(Th+-N) = 6.69 ± 0.35 eV, D0(Th+-O) = 8.40 ± 0.28 eV, and D0(Th+-C) = 3.50 ± 0.18 eV. In addition, cross sections for the reactions of ThO^+ with N_2, O_2, CO_2, and CO data have been collected, but not yet analyzed.

Spectroscopic work in the Morse group has concentrated on the construction of a cryocooled 22-pole ion trap photodissociation spectrometer. At this point, our electron impact ion source, quadrupole mass filter, and Daly detector are working well. We are currently installing a quadrupole beam bender to direct the ions into the 22-pole trap, which is also currently being assembled. We are also adding a separate cryopump upstream of the cold 22-pole trap, to remove condensable gases before they freeze onto the cryo-cooled 22 pole assembly. Within the next month we will begin spectroscopic studies of UN, UN_2, and ThO_2 using the existing resonant two-photon ionization and laser-induced fluorescence instruments.

Matrix Infrared Spectroscopic and Computational Investigations of Novel Small Uranium Containing Molecules

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Funding:	$120,000

OVERALL RESEARCH GOALS

Our goals include matrix infrared spectroscopic and density functional computational investigations on new small molecules containing uranium, thorium, and lanthanide atoms.

SIGNIFICANT ACHIEVEMENTS DURING 2009 - 2011

Laser evaporation of carbon rich uranium/carbon alloy targets into condensing argon or neon matrix samples gives weak infrared absorptions that increase on annealing, which can be assigned to new uranium carbon bearing species. New bands at 827.6 cm^{-1} in solid argon or 871.7 cm^{-1} in neon become doublets with mixed carbon 12 and 13 isotopes and exhibit the 1.0381 carbon isotopic frequency ratio for the UC diatomic molecule. Another new band at 891.4 cm^{-1} in argon gives a three-band mixed isotopic spectrum with the 1.0366 carbon isotopic frequency ratio, which is characteristic of the anti-symmetric stretching vibration of a linear CUC molecule. No evidence was found for the more stable cyclic U(CC) isomer. Other bands at 798.6 and 544.0 cm^{-1} are identified as UCH, which has a uranium-carbon triple bond similar to that in UC. Evidence is found for bicyclic $U(CC)_2$. This work shows that U and C atoms react spontaneously to form the uranium carbide U=C and C=U=C molecules with uranium-carbon triple bonds.

Laser-ablated lanthanide metal atoms were condensed with CH_2F_2 in excess argon at 6 K or neon at 4 K. New infrared absorption bands are assigned to the oxidative addition product methylene lanthanide difluorides on the basis of deuterium substitution and vibrational frequency calculations with density functional theory (DFT). Two dominant absorptions in the 500 cm^{-1} region are identified as lanthanide-fluoride stretching modes for this very strong infrared absorption. The predominantly lanthanide–carbon stretching modes follow a similar trend of increasing with metal size and have characteristic 30 cm^{-1} deuterium and 14 cm^{-1} ^{13}C isotopic shifts. The electronic structure calculations show that these CH_2LnF_2 complexes are not analogous to the simple transition and actinide metal methylidenes with metal–carbon double bonds that have been investigated previously; the lanthanide metals (in the +2 or +3 oxidation state) do not appear to form a π-type bond with the CH_2 group. The DFT and ab initio correlated molecular orbital theory calculations predict that these complexes exist as multi-radicals, with a Ln-C s bond and a single electron on C-2p weakly coupled with fx (x = 1 (Ce), 2 (Pr), 3(Nd), etc.) electrons in the adjacent Ln-4f orbitals. The Ln-C s bond is composed of about 15% Ln-5d,6s and 85% C-sp^2 hybrid orbital. The Ln-F bonds are almost purely ionic. Accordingly, the argon-neon matrix shifts are large (13-16 cm^{-1}) for the ionic Ln-F bond stretching modes and small (1 cm^{-1}) for the more covalent Ln-C bond stretching modes.

Reactions of laser-ablated U atoms with N_2 and H_2 mixtures upon co-deposition in excess argon at 5 K gave strong NUN and weak UN infrared absorptions and new bands at 3349.7, 966.9, 752.4, and 433.0 cm^{-1} for the unusual new U(V) molecule N=U=N-H, uranimine nitride, containing both triple and double bonds. This identification is based on D and ^{15}N isotopic substitution and comparison with frequencies computed by density functional theory for the $^{2}\Delta$ ground state NUNH. Calculated bond lengths are compared to those of the $^{1}\Sigma_g^+$ ground state of U(VI) uranium dinitride N=U=N, the $^{2}\Phi$ ground state of the isoelectronic nitride oxide N=U=O, and the ^{3}A ground state of the U(IV) uranimine dihydride $HN=UH_2$ molecule, which have all been prepared in solid argon matrices in this laboratory. Mulliken bond orders based on the CASSCF orbitals for N=U=N-H are 2.91, 2.19, and 1.05, respectively. Here the terminal nitride is effectively a triple bond just as found for N=U=N. The solid argon matrix is a convenient medium to isolate reactive terminal uranium nitrides for examination of their spectroscopic properties.

OBJECTIVES FOR 2011-2012

Our objectives for this fiscal year include completing the reactions of U, Th, and Ln metal atoms with methanol and dimethyl ether. The $CH_3U(O)H$ and $(CH_3)_2UO$ molecules will be prepared and compared to the H_2UO product from the water reaction.

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:	2 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding:	$150,000

The goal of the proposed research is to define the extent of hydration and covalency of the f-element cations in aqueous and mixed solvent electrolyte systems using an integrated experimental and computational approach. We propose to study mixed solvents where the solvent di-electric constant can be varied systematically. The specific objectives of these studies are to:

(1) explore the effect of solvent properties, cationic radius, and covalency for the f-element cations on solubility, hydration, and coordination geometry for solution species; and

(2) represent the correlation between changes in cation hydration and solvent properties with solution speciation in thermodynamic modeling tools.

Once the hydration characteristics of the f-elements and their complexes are defined, f-element separations based on “tunable solvents” become possible.

Using experimental and computational methods, we will determine the extent of water solvation about the f-element metal center, the contributions of inner- and outer-sphere coordination as a ligand is added, and the extent of covalency in the complex (where relevant) as the solvent dielectric constant changes. The primary focus of our work will be on the trivalent lanthanides and actinides, but we will also consider the actinyl cations. The cations of interest include La^{3+}, Eu^{3+}, and Lu^{3+} (which provide a range of cationic size for the ionic 4f elements), Am^{3+} and Cm^{3+} (which provide the possibility for covalent character in complexation along with a difference in cationic size), and the actinyl cations $NpvO_2^{+}$ and $UVIO_2^{2+}$ (which provide an opportunity to explore effects from varying actinide oxidation states and the role of the dioxo O atoms). Binary solvent systems (e.g., methanol: water (MeOH:water) and dimethylsulfoxide:water (DMSO:water)) under variable electrolyte compositions will be used. Finally, simple ligands will be used: acetate and alpha-hydroxyisobutyrate. We will combine indirect (e.g., solubility, distribution methods, calorimetry) with direct spectroscopic methods (e.g., fluorescence, UV-VIS-NIR, NMR, EXAFS, neutron scattering) to determine numbers of water and non-aqueous solvent molecules associated with the f-element cation centers as the solvent composition is varied.

Origin of Actinide Ion Partitioning in Biphasic Systems

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Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$200,000

The goal of the work is to provide a chemical description of the multiple forces that contribute to heterogeneous solvent organization and ion extraction at length scales accessible by quantum mechanical and statistical mechanical methods. A fundamental understanding of ion extraction mechanisms will enable the exploitation of "phase phenomena" to achieve more efficient, predictable, and controllable separation processes. We utilize a synergistic approach composed of simultaneous density functional theory (DFT) calculations and molecular dynamics (MD) simulations that respectively provide electronic structure and ensemble correlations of molecular systems. These studies are engaged in a feedback loop to yield a self-consistent description of prototypical actinide ions (e.g., Np) and their chelates (acetylacetate ion) in aqueous and organic media as well as at the liquid:liquid phase boundary.

Significant achievements during 2011 include the following objectives that have been pursued:

- Characterize the supramolecular chemistry of exemplary spherical (trivalent) and linear di-oxo (hexavalent) Np ions in pure water and alkane solvents, including solvent exchange and complexation reactions with prototypical acetylacetone (acac) ligands substituted with hydrophobic and hydrophilic substituents.
- Determine the interfacial structure of water:alkane mixtures as a function of alkane packing, varying concentrations of extracting acac ligands, and proximity of solutes to the interface.
- Describe the transport process of Np(III) and $Np(VI)O_2^{2+}$ and their acac complexes across water:alkane interfaces, and determine the influence of (1) interfacial order and packing of the alkane, and of (2) hydrophobic and hydrophilic solvation characteristics on transport properties.

To date significant achievements have been made on each objective. (1) Density functional theory studies were first performed so as to benchmark the interaction potentials of the ion with water and organic solvents against more highly accurate MP2 and DF-LPM2 methods. DFT studies were then performed examine the solvation of Np(III) and Np O_2^{2+} in both aqueous and organic media. Significant charge polarization is observed across aqueous solvation shells for both metal ions, which is absent in organic media, however the conformational flexibility of the alkane solvent significantly impacts its solvation structure. The benchmarked DFT data (along with MP2) is currently being used to fit classical polarizable interaction potentials using the ForceFit program. (2) Similar computational benchmarking (but including CCSD(T) methods) has been performed for the interaction potentials of water with pentane and neopentane organic solvent molecules. In this context dispersion corrected density functionals have been very successful in correctly describing the weak attractive interaction and thus have been used to examine the solvation of single water molecules by organic solvents and vice versa. This has allowed us to determine thermodynamic properties of solvation that are relevant at a dynamic oil:water interface. These DFT methods will be used in further periodic boundary DFT calculations. In parallel, classical molecular dynamics simulations are being performed to further explore the dynamical features of the oil:water interface as a function of the conformational flexibility of the organic solvent (chain pentane vs. neopentane). In particular, we are focusing upon the calculation of radial distribution functions, density profiles, diffusion coefficients, the surface tension at the interface, and the free energy of permeation across an interfacial boundary of both water and organic solvents. (3) Initial DFT calculations have been performed that examine the thermodynamic and structural features of Np(III) and Np O_2^{2+} complexes with extracting acetylacetate ligands. Very good agreement has been obtained with available experimental data and is being used to ascertain the most likely metal-complexes in aqueous and organic solutions. (4) The upcoming scientific accomplishment made on the project rely heavily on analyses of data from molecular dynamics simulation. We have developed a method for post-processing that uses the tools of graph theory and network analysis to explore and characterize the H-bond network of liquid water. By treating individual molecules as vertices and H-bonds as edges, we obtain information about connectivity and supramolecular structure of water in the bulk, around solutes, and at interfaces.

DOE National Laboratories

An Integrated Basic Research Program for Advanced Nuclear Energy Separations Systems Based on Ionic Liquids

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Sr. Investigator(s):	Shkrob, Ilya, ARGONNE NATIONAL LABORATORY Chemerisov, Sergey, ARGONNE NATIONAL LABORATORY
Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$200,000

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 that are meeting these challenges, as these new solvents offer non-volatility, non-flammability, high conductivity, and wide electrochemical windows. These applications involve exposure of the solvent to radiation generated by decaying radionuclides, which is a major concern about these solvents. Argonne's goal is to delineate 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. Magnetic resonance, x-ray spectroscopy, product analyses, measurements of partitioning coefficients, and other methods are used to this end. We study radiolytic damage of neat ionic liquids and also the extracting agents, ionophores, and solvent modifiers in these liquids. In FY 2011 the focus of our studies is the chemistry of ion fragmentation and the ensuing radical reactions in radiolysis of aliphatic and aromatic ILs, assessing the relative stability of different classes of the ILs, assessing the effects of the extracted nitric acid on this chemistry, discovering ways to mitigate the radiation damage, and studying radiation-induced degradation of crown ethers and related ionophores. Our research resulted in eight publications with three publications in the works. Our greatest success so far was the discovery of a class of the practically important ILs that exhibit exceptional radiation stability, these being the ILs that are based on 1,2-benzenedisulfonimide anion.

Heavy Element Chemistry/Separations Science and EMSI – Actinides in the Environment

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Wilson, Richard, ARGONNE NATIONAL LABORATORY
Students: 5 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $3,035,000

This program is focused on developing a fundamental understanding of the chemical and physical properties that characterize the interaction of an actinide ion with its surrounding environment. Viewed broadly from a metal-separations perspective, our approach involves the determination of the relative roles played by coordination environment and metal-ligand interactions, occurring at varying length scales, on the stability and reactivity of the f ion. Within this framework the need for basic structural information, including preferred coordination numbers and geometries, is addressed through a robust effort to synthesize and characterize new materials, notably extended solids and coordination compounds. The influence of crystalline length scale, lattice dimensionality, and bonding on the electronic and magnetic properties exhibited by f ions in these solids constitutes a central theme. Complementing this materials approach are efforts to understand local coordination structures in solution and their influence on system energetics. Novel to this program is research centered on characterizing intermediate-length-scale correlations and their impact on separations, notably in the organic phases of solvent extraction systems. These studies are revealing the interrelationship of the physical and chemical properties of complexes, ligand donor and structural characteristics, and solvation effects using spectroscopic, thermodynamic, kinetic, and synchrotron-based techniques. Our expertise in working with transuranic samples in the Advanced Photon Source User Program is made available to any user through the Actinide Facility.

Understanding Actinide Aggregation

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Sr. Investigator(s): Dixon, David, ARGONNE NATIONAL LABORATORY
Students: 3 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $744,000

The ultimate goal of the proposed work is the development of a predictive understanding of the formation, structures, stabilities, and reactivities of complex actinide aggregates forming under conditions relevant to the reprocessing of used nuclear fuel. Insight is sought to inform the design of separations processes specifically targeting such species. To accomplish this goal, we are employing a multifaceted approach that combines new advances in the experimental determination of metal-ion speciation, coordination and stability in solution with a mechanistic synthetic approach, and recent developments in computational chemistry. This combination of strategic capabilities permits the acquisition of new knowledge about the solution chemistry underlying metal-aggregate formation and stability. This approach is affording original insights and theories of actinide nanophase formation that will form the basis upon which to design novel approaches for 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.

An Integrated Basic Research Program for Advanced Nuclear Energy Separations Systems Based on Ionic Liquids

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Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $551,000

If nuclear power is to play a major role in serving the world’s growing energy needs, 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. We expect that ionic liquids (ILs, salts that melt at low temperatures) will enable separations 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 heavy element 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 heavy element separations chemistry. The goal is to replace current technologies with ones that allow more efficient use of resources and smaller environmental impacts.

Actinide Chemistry

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Students:	3 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$2,500,000

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 (ANES), 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, which includes a better understanding of f-orbital bonding, exploiting f-orbital bonding for improved separations, controlling the chemistry of the problematic radionuclides 237Np and 99Tc, and experimentally quantifying radiation damage in actinide materials to compare these quantities to theory.

Exploring f-element Science with Gas-phase Atomic, Molecular, and Cluster Ions: A Link between Actinide Chemistry in Condensed and Gas Phases

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Principal Investigator:	Gibson, John K.
Sr. Investigator(s):	
Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$500,000

The broad goal is to use advanced gas-phase ion experimental techniques to examine fundamental aspects of 5f-element chemistry. The focus is on the technologically problematic and scientifically interesting mid-series actinides, U, Np, Pu, Am and Cm; studies will also be carried out with selected 4f-elements such as Ce. The types of investigations being proposed represent a far-reaching extension of previous types of gas-phase ion chemistry studies that have been carried out with these actinides and related materials. Central objectives include gaining fundamental understanding of actinide chemistry in elementary molecular species, in aqueous and non-aqueous solutions, in aggregates such as polymers and other nanoparticles, and at interfaces of direct relevance to such processes as gas-solid reactions and particulate growth.

Meeting the Challenges Posed by Advanced Nuclear Energy Systems: Understanding Cont. Actinide and Fission Prod. Chem. an Radiation Effects in Actinide

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Sr. Investigator(s):	Andersen, Richard A., LAWRENCE BERKELEY NATIONAL LAB Booth, Corwin H., LAWRENCE BERKELEY NATIONAL LAB Gibson, John K., LAWRENCE BERKELEY NATIONAL LAB Lukens, Wayne W., LAWRENCE BERKELEY NATIONAL LAB Rao, Linfeng, LAWRENCE BERKELEY NATIONAL LAB Raymond, Kenneth N., LAWRENCE BERKELEY NATIONAL LAB
Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$814,000

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 (ANES), 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

(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 237Np and 99Tc, and experimentally quantifying radiation damage in actinide materials to compare these quantities to theory.

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), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$500,000

The aim of the proposed research is to develop transformative knowledge about the extent to which covalent interactions are important in actinide bonding with soft donor atom ligands. Syntheses, structural, spectroscopic and theoretical analyses will be used to unravel the relative roles of the metal valence f and d orbitals and quantify their overlap with ligand based orbitals. The focus will be upon studying the transuranic metal ions as this is where contemporary experimental knowledge is most lacking. By carrying the investigation across the 5f series the work will be able to definitively establish bonding trends with soft donors for all the relevant actinide ions, in all relevant oxidation states. The results will provide a knowledge driven basis for the future design of advanced separations in next generation fuel cycles. It is expected that we will gain detailed knowledge of how basic chemical bonding principles such as structure, bond strength, covalency, and ligand donor type can be manipulated to effect preferential bonding for actinide ions over lanthanide ions.

Heavy Element Chemistry

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Sr. Investigator(s):	Wilkerson, Marianne, LOS ALAMOS NATIONAL LABORATORY Kiplinger, Jackie, LOS ALAMOS NATIONAL LABORATORY Morris, David, LOS ALAMOS NATIONAL LABORATORY Conradson, Steve, LOS ALAMOS NATIONAL LABORATORY Martin, Rich, LOS ALAMOS NATIONAL LABORATORY Batista, Enrique, LOS ALAMOS NATIONAL LABORATORY Kozimor, Stosh, LOS ALAMOS NATIONAL LABORATORY
Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$1,325,000

The central goal of the LANL Heavy Element Chemistry program is to advance the understanding of fundamental electronic structure and bonding in actinide materials. Our interdisciplinary, multi-method approach uses modern synthetic methodologies, sophisticated spectroscopic characterization, and advanced theory and modeling to characterize (and ultimately predict) the chemical behavior of the actinides under a wide range of conditions, from their speciation in aqueous media to their structural behavior in solid matrices. Emphasis is placed on the development of new spectroscopic, structural, and theoretical tools to understand and predict physical and chemical behavior in a range of environments. These efforts provide the science base to meet the next generation of needs in actinide science within the DOE complex. Investigation of the speciation and coordination chemistry of the light actinides in aqueous media can address problems in long-term site stewardship and response to radiological releases (predicting environmental fate and transport and devising new solutions for remediation), as well as advance our ability to detect and identify the chemical history of uranium, neptunium, or plutonium. Non-aqueous coordination and organometallic chemistry provides access to the broadest possible set of ligands with which to test predictive models of chemical behavior.

An Integrated Basic Research Program for Advanced Nuclear Energy Separations Systems based on Ionic Liquids

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$207,000

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 part of a project lead by James Wishart at BNL that lies in development of ionic-liquid systems for separation of fission products and collaboration with Professor Charles Hussey for electroseparation of fission products via ionic liquids.

Influence of Solution Phase and Interfacial Structure on Stability of Actinide Oxidation States: A Computational Approach

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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$295,000

Knowledge of the oxidation states of actinide elements in liquid or solid phases or at interfaces, and the ability to predict, control, or manipulate them is critical to virtually all aspects of environmental actinide chemistry, waste processing, and separations. It is clear that a fundamental understanding of the mechanisms of actinide oxidation/reduction is a key factor in actinide solution and interfacial chemistry. With the availability of high performance parallel computational resources and scalable software, computational chemistry can be used to study actinide oxidation states at various interfaces and in the presence of multiple ligands in solution, and to obtain a basic understanding of actinide oxidation/reduction (redox) reactions. Computational chemists can address questions such as *How does a local molecular environment such as a solvent or an interface affect the actinide oxidation state and its redox (or electron-transfer) mechanism?* and *What is the oxidation state of actinide phases at an interface?* To answer these questions, it is essential to understand fundamental questions such as *How do 5f electrons participate in bonding? What is the ground-state multiplet structure?* and *How important are spin-orbit effects?* We propose to study the influence of environments on redox mechanisms and oxidation states of actinides in solution and solid phase, and at interfaces. We propose to use the latest developments in Gaussian and plane-wave density functional theory in combination with the zeroth order regular approximation for relativistic scalar and spin-orbit effects, and we will properly account for the molecular environments. These studies will provide new insights and a fundamental understanding of actinide redox mechanisms, and can aid in the development of strategies to immobilize actinides and in the design of new compounds for efficient separation of actinides.

Photosynthetic Systems

Institutions Receiving Grants

Optimizing Rubisco Regulation for Increased Photosynthetic Performance under Climate Change	
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Principal Investigator:	Salvucci, Michael
Sr. Investigator(s):	
Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$127,000

Photosynthesis is acutely sensitive to inhibition by moderate heat stress because of the thermal sensitivity of Rubisco's catalytic chaperone, Rubisco activase. The broad objectives focus on improving the performance of photosynthesis, particularly under moderate heat stress by: (1) introducing more a 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. Under objective 1, 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. Transformation of camelina with cotton and rice Rubisco activase is in progress. Under Objective 2, experiments comparing the effect of ADP on Rubisco activase activity showed that the non-redox regulated form of Rubisco activase in tobacco differed from this form in Arabidopsis and camelina. Unlike in Arabidopsis and camelina, this form from tobacco exhibited sensitivity to inhibition by ADP even in the absence of the redox-regulated form. 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. This control of photosynthesis by Rubisco activase is being used to design plants that respond quicker to rapid changes in irradiance level.

Chlorophyll Synthesis and Stability in Cyanobacteria

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Sr. Investigator(s):	
Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$170,000

In the grant period that was recently completed, a main objective of the project was to understand the interrelationships between chlorophyll (and its synthesis), chlorophyll-binding proteins, and thylakoid membrane formation. Using stable-isotope labeling followed by mass spectrometry, we monitored the rate of disappearance of "old" chlorophyll and chlorophyll-binding proteins, and measured the rate of biosynthesis of "new" pigment and proteins associated with the two photosystems. For these and other studies, we used the cyanobacterium Synechocystis sp. PCC 6803, which easily takes up relevant stable isotope-labeled compounds and for which we have generated mutants that lack specific photosystem components.

Now that we have set up a system to distinguish between old and newly synthesized membrane components, we are extending these studies to understand thylakoid membrane biogenesis. Very little is known about how thylakoid membranes are formed, but it is clear that chlorophyll is required in both plants and cyanobacteria, for reasons as yet unknown. Another question is how thylakoids are formed and how new proteins are inserted, as we do not see a large number of ribosomes associated with either thylakoid or cytoplasmic membranes in cyanobacteria. One hypothesis is that membranes are formed from vesicles that in turn are synthesized de novo or bud off from existing membranes. One protein that may be relevant in this respect is VIPP-1 (vesicle-inducing plastid protein-1), which upon overexpression, causes an increase in the number of thylakoid membranes per cell. However, we are also focusing on several other proteins that may be involved with induction of vesicles or with protein integration into membranes. We are using a combination of genetic, biochemical, and ultrastructural approaches to determine how membranes are formed. This is a long-standing problem that has proven to be very difficult to solve over the years, but we think that we have the right combination of expertise and approaches to contribute significantly to a solution.

The Regulation of Carbon Fixation in Plant and Green Algae: Rubisco Activase and the Origin of Heat Inactivation of CO_2 Assimilation

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Funding:	$250,000

To better understand the ATP-driven regulation of carbon assimilation, we are using biophysical methods to study the structure and function of higher plant Rubisco activase. The rapid release of tight-binding inhibitors from dead-end Rubisco complexes requires the activity of activase, an AAA+ ATPase that utilizes chemo-mechanical energy to open closed Rubisco sites. Activase is thought to play a central role in coordinating the rate of CO_2 fixation with the light reactions of photosynthesis, and has been proposed to modulate the thermotolerance of photosynthesis. The objectives of the DOE funded project are to (1) determine the denaturation temperatures of higher plant activases by means of circular dichroism spectroscopy, (2) solve X-ray structures of full-length activases or structural domains, and (3) elucidate the activase self-association mechanism by single-molecule spectroscopic methods and analytical ultracentrifugation.

Protein Targeting to the Chloroplast Thylakoid Membrane: Structure and Function of a Targeting Complex

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Funding:	$165,000

OVERALL RESEARCH GOALS

The research objectives are to understand the structure based mechanism by which the chloroplast signal recognition particle (cpSRP) and its receptor (cpFtsY) direct light harvesting chlorophyll binding proteins (the LHCs) to Albino3 (Alb3), an insertase required for LHC insertion into chloroplast thylakoid membranes. We hypothesize that binding of cpSRP43 subunit 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. We are testing this hypothesis by (1) identifying loss-of-function mutations in Alb3 C-terminal peptide that eliminate its ability to (a) bind cpSRP43 and (b) stimulate GTP hydrolysis by cpSRP/cpFtsY, (2) using NMR to determine the structure of Alb3 Cterm alone and bound to the Ank-CD2 domain of cpSRP43, and (3) examining how interaction between cpSRP43 and the C-terminus of the Alb3 insertase promotes unidirectional transfer of LHC targeting substrates from cpSRP to Alb3.

Completion of the proposed studies will provide structural and functional details that are missing in our understanding of membrane events required for LHC insertion. Additionally, our results will set the stage for future studies aimed at addressing the potential for post- and co-translational targeting mechanisms to converge at Alb3 through binding of cpSRP43 (post-translational) or chloroplast ribosomes (co-translational) to the Alb3 C-terminus. It is also expected that the proposed work will have a general impact on understanding insertase activity of Alb3 homologues in bacteria, which are required for biogenesis of energy generating complexes in bacteria, which are being developed for biofuel production.

SIGNIFICANT ACHIEVEMENTS 2010 - 2011

Our data show that efficient association of Alb3 with cpSRP/cpFtsY relies on cpSRP43, a novel cpSRP subunit thought previously to function primarily in the soluble phase of protein targeting through its ability to bind LHCP and the GTPase subunit cpSRP54. The role of cpSRP43 in promoting association between Alb3 and soluble targeting components relies on high affinity of cpSRP43 for Alb3. The Ankyrin-repeat region of cpSRP43 interacts directly with the stroma-exposed Alb3 C-terminus. Alb3-Cterm peptide, which binds cpSRP43 (or the Ankyrin domain of cpSRP43) with nM affinity, promotes GTP hydrolysis by cpSRP54/cpFtsY only in the presence of cpSRP43. Importantly, mutational analysis of cpSRP43 demonstrates that its cpSRP54-binding domain (chromodomain 2) is needed to observe GTP hydrolysis in the presence of Alb3-Cterm peptide. In addition, Alb3-Cterm peptide appears to promote LHCP release from cpSRP. Taken together, our data supports a model (see below) in which cpSRP43/Alb3-Cterm interaction at the membrane is directly involved in release of LHC from cpSRP and initiates GTP hydrolysis by cpSRP/cpFtsY, an event that is required to recycle cpSRP and its receptor for subsequent rounds of targeting.

SCIENCE OBJECTIVES FOR 2011 - 2012

(1) With the HSQC spectrum of cpSRP43 Ankyrin domains nearly complete, we will be able to use peak shift perturbation assays to identify amino acids in the cpSRP43 Ankyrin-repeat domain that interact with residues of the Alb3 C-terminus. The cpSRP43 mutants designed from these studies are anticipated to lack Alb3 binding and lack the ability to release LHCs from cpSRP.

(2) Using ITC and HSQC data from NMR studies, we will examine Alb3-Cterm mutants for loss of binding to cpSRP43 and loss of GTPase stimulation. These Alb3-Cterm mutants, as recombinant proteins, are also expected to lack the ability to stimulate LHC release from cpSRP.

Chloroplast Antisense RNAs and Post-Transcriptional Gene Regulation

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Our project aims to characterize the diversity and functions of non-coding RNAs (ncRNAs) in chloroplasts, an RNA class which is abundant but poorly understood in organelles, with a particular focus on antisense RNAs (asRNAs). Our experimental goals are: (1) to identify the full complement of chloroplast-encoded asRNAs, and address their biological functions; (2) to understand how certain asRNAs are selectively accumulated, given that the entire chloroplast genome is fully transcribed on both strands; and (3) to explore roles of two chloroplast ribonuclease III (RNC) homologs in their possible metabolism of double-stranded sense-antisense RNA duplexes.

The implications of this work for energy biosciences arise from the fact that the chloroplast is where photosynthesis occurs, and thus where solar energy is stored as chemical energy. The chloroplast has its own genes, and numerous studies have shown that the regulation of these genes can grossly affect the photosynthetic output of an organism, and how it responds to environmental stress. Our focus on ncRNAs derives from the fact that this is a class of regulatory molecules only recently identified, for which little functional information is available. The many efforts to use chloroplast engineering to achieve applied goals will need to be cognizant of this regulatory framework, among others.

Regulation of Plant Cells, Cell Walls, and Development by Mechanical Signals

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The objective of the research being conducted is to use live imaging, genetic and environmental alterations, and computational modeling to understand how plant cells communicate in the Arabidopsis shoot apical meristem. As the shoot apical meristem is the site where leaves and flowers first form, this cell-cell communication sets the patterns of growth for the above-ground plant, including those parts that are used for both starch-based and cellulose-based biofuels, and for seed-based biodiesel.

It has long been known that there are chemical signals in the shoot apical meristem, most saliently signaling by the plant hormone auxin, which regulates the pattern in which leaves and flowers are formed, and the local rates of cell division. Our recent work adds to the chemical signals physical (mechanical) signals. We have shown that plant cells in the shoot apical meristem can respond directionally and locally to mechanical stress by reorganizing their microtubule cytoskeletons such that the cortical microtubule bundles are parallel to the principal direction of anisotropic stress. This has implications for cell wall synthesis, as the direction in which newly synthesized cellulose fibrils are deposited in the cell wall is determined by the cortical microtubule array.

In the past year we have shown that the direction of auxin transport from these cells is highly correlated with microtubule direction, and therefore that the direction of auxin flow responds to physical stress. An early effect of auxin on plant cells is increased cell wall viscoelasticity, and thereby increased cell expansion, which in turn feeds back upon the stress pattern, as local cell enlargement stresses the neighboring cells. We have therefore uncovered a supracellular feedback mechanism in which shoot apical meristem cells use auxin and mechanical signaling feeding back upon each other, with auxin determining the sites of cell enlargement (and therefore cell division), and mechanical signals determining the cellulose reinforcement direction of the cells as they expand and synthesize new cells walls. This reinforcement directionally resists stress, thereby changing the stress pattern, and therefore changing the new directions of cellulose deposition, and the new directions of auxin transport.

Experiments now in progress are directly testing the implications of this model, and allowing the creation of computational models of the complex feedbacks involved. Such computational modeling of stress patterns and hormone transport in plant tissues is leading to predictive models of cell wall synthesis and plant growth. These models in turn are informing our ability to design and grow plants with novel architectures, and with higher production of cell walls and cellulose.

Structural and Kinetic Studies of Novel Cytochrome P450 Small-Alkane Hydroxylases

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Funding:	$80,000

We are investigating the structures, biophysical properties, and kinetics of members of two families of cytochrome P450s that have been evolved in the laboratory to catalyze the hydroxylation of gaseous alkanes. Activity towards propane, ethane, and methane have not been previously reported for any naturally-occuring cytochrome P450, yet we have shown that highly proficient small-alkane P450 hydroxylases are possible and, indeed, easily accessible by mutation from existing P450s. One laboratory-evolved enzyme, derived from the fatty acid hydroxylase P450 BM3 (CYP102A1 from Bacillus megaterium), inserts oxygen primarily at the 2-position of propane. We also found a member of the newly-characterized longer-chain alkane hydroxylase CYP153 family, CYP153A6 to hydroxylate propane and butane and do so primarily at the energetically disfavored terminal carbon (1-position). These heme enzymes are unrelated mechanistically and evolutionarily to the monooxygenases that are known to hydroxylate C1-C4 alkanes in alkanotrophic organisms and therefore offer a new mechanism and catalytic platform for selective oxidation of small alkanes.

With a collection of small alkanes hydroxylating cytochrome P450s, we are able to investigate differences between the active oxidants generated within the enzymes that are responsible for catalysis. By studying the reactivity of enzyme oxidants generated chemically, we can determine the substrate range of the active catalyst independent of the substrate recognition limitations of the enzyme fold. This basic understanding will aid further evolution or design of a possible methane-hydroxylating cytochrome P450 and P450 catalysts for selective alkane oxidation. It will also provide inspiration for future design of new biomimetic catalysts for these key conversions, including the conversion of methane to methanol. We have also obtained the x-ray crystal structure of a key evolutionary intermediate along the pathway to the propane-hydroxylating P450 BM3. This structure helps to explain the broad substrate specificity of this intermediate, which allows it to be optimized by directed evolution for activity on substrates that range from propane to large pharmaceutical molecules.

Phytochrome from Green Plants: Properties and Biological Function

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Funding:	$160,000

OVERALL RESEARCH GOALS

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 goal 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 goal, the specific aims for this funding period are to (1) delineate the biological functions of the multiple known 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 chromatin immunoprecipitation (ChIP) procedures to identify promoters that are potential direct targets of these phy signaling partners. We are using two primary general strategies to approach these objectives: (1) genetic approaches, including structured mutational analysis of the potential roles and interactions among the known PIF proteins in the SAR, and (2) genomic approaches, including integrated genome-wide expression profiling and ChIP analyses aimed at identifying direct, primary targets of the PIF-bHLH transcription factors in the phy-regulated transcriptional network.

SIGNIFICANT ACHIEVEMENTS 2010-2011

Plants respond to light signals informing them of imposed or impending vegetative shade, via the phytochrome (phy) photoreceptor system, by adaptive changes in growth and development, collectively termed the Shade Avoidance Response (SAR). To examine the roles of the PIF1, 3, 4 and 5 bHLH factors in transducing this perceived information to the transcriptional network, we compared the genome-wide transcription profiles of wild-type and quadruple pif (pifq) mutants in response to shade. The data identify a subset of genes, enriched in transcription-factor-encoding loci, that respond rapidly (within 1 h), in a PIF-dependent manner, to the shade signal, and that contain promoter-located G-box-sequence motifs (CACGTG), known to be preferred PIF binding sites. These genes are thus potential direct targets of phy-PIF signaling that function in the primary transcriptional circuitry that controls downstream response elaboration. A second subset of PIF-dependent, early-response genes, lacking G-box motifs, are enriched for auxin-responsive loci, suggestive of being indirect targets of phy-PIF signaling involved in the rapid cell-expansion responses known to be induced by shade. A meta-analysis comparing deetiolation- and shade-responsive transcriptomes identifies a further subset of G-box-containing genes that reciprocally display rapid repression and induction in response to light and shade signals at the inception of deetiolation and shade-avoidance, respectively. Collectively, these data define a core set of transcriptional and hormonal (auxin, cytokinin) processes that appear to be dynamically poised to react rapidly to changes in the light environment in response to perturbations in the mutually antagonistic regulatory activities of the phys and PIFs.

Analysis of Proteins Affecting Chloroplast Function

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The capture of light energy into chemical energy and the production of plant biomass for biofuels depend on the optimal development and functioning of the plant chloroplast, the site of these activities. Chloroplasts contain DNA and can synthesize some proteins; however, most chloroplast-localized proteins are nuclear-encoded, synthesized in the cytosol, and imported into the chloroplast. The chloroplast has to coordinate the synthesis of its own protein products with that of the nuclear-encoded proteins and, additionally, synthesis has to match the developmental and metabolic demands. Light energy and electron flow also damage the photosynthetic apparati, and synthesis occurs to replace damaged proteins. Thus, even mature, non-dividing chloroplasts require regulated transcription, RNA processing, and translation to produce those components that need replacement, and this must be coordinated with nuclear-encoded imported proteins. The objectives of this research were to characterize the biological functions of two related nuclear-encoded proteins (FLN1 and FLN2) whose loss in the model plant *Arabidopsis thaliana* result in a chlorotic phenotype as seedlings. These proteins localized to transcription complexes in chloroplasts. Interestingly, these proteins are not known transcription factors, but members of a family of carbohydrate-like kinases, called pfkB carbohydrate-like kinases, and their biochemical activity is unknown.

Toward understanding their in vivo function, we studied the phenotype of plants lacking expression of either At3g54090 (gene name *FLN1*) or At1g69200 (gene name *FLN2*). We characterized multiple T-DNA insertion alleles for *FLN2* and showed they had the same phenotype, retained with backcrossing to wild type. Only a single mutant *fln1* T-DNA insertion allele was available; however, the expression of a transgene in the *fln1* mutant background restored the plant to a wild-type phenotype, proving that the insertion in *FLN1* was responsible for the phenotype. Loss of either *FLN1* or *FLN2* results in chlorotic plants that differ in severity. On soil, both mutants germinate with small yellow cotyledons. *fln2* mutants green slowly, develop true leaves, and eventually flower, producing viable seed. In contrast, *fln1* plants never green and die soon afterwards. *fln1* plants can develop true leaves when grown on a synthetic media with exogenous sugar; however, they remain white. Dark grown mutants are similar to wild type, indicating skotomorphogenesis is normal. The ultrastructure of chloroplasts was examined at the EM level, and despite normal cell expansion in the dark, etioplast morphology was not. *fln2-1* etioplasts did contain prolamellar bodies, but these were atypical and lacked any obvious associated stromal thylakoids that are normally found in wild type. Chloroplasts of light-grown *fln1* were more abnormal than *fln2*, correlating with the severity of the phenotypes. To test whether the two FLN proteins function similarly but with different impacts, we crossed *fln1* and *fln2* mutants and correlated the phenotype of the resulting progeny with their *FLN1* and *FLN2* genotypes. These studies revealed haploinsufficiency that is increased in severity with loss of each wild type copy, and that when both loci are homozygous for their respective insertions, there is no further growth passed cotyledon expansion and production of two small unexpanded first true leaves. We were unable to constitutively over-express these proteins, but we developed dexamethasone-inducible *fln1* expression lines. We will use this inducible expression system to test the requirement for certain conserved domains of the FLN proteins. In summary, we have characterized loss of function mutants in two pfkB type carbohydrate kinases and demonstrate their essential role in chloroplast and leaf development.

Energetics and Mechanisms of Protein Transport Across Chloroplast Membranes

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Funding:	$80,000

This project seeks to elucidate the mechanism of operation and energy requirements for chloroplast protein targeting. To this end we have measured the amount of ATP hydrolyzed per protein imported into the plastid across the envelope membranes, the import of a folded protein into the plastid, examined the role of VIPP1 in thylakoid protein transport, and have successfully placed a pH-dependent GFP into both the chloroplast stroma and thylakoid lumen that will be used to monitor light-induced pH changes.

Much is known about the types of energy inputs required for the cell's considerable protein trafficking activity, but the quantitation of the amount of energy required for these processes has received little attention. In a past DOE funding period we determined that the cost of protein transport on the cpTat pathway exceeded the equivalent of 10,000 ATP molecules hydrolyzed per protein transported. During this funding period we have measured the amount of ATP hydrolyzed as a protein is imported across the plastid envelope membranes into the stroma. Using two different precursors synthesized by three different techniques we have found the cost of the import reactions to be approximately 600 ATP molecules hydrolyzed per protein imported.

VIPP1 is a multi-function protein present in different locations in the chloroplast. Its addition causes a stimulation of protein transport on the cpTat pathway, and we have examined the mechanism through which this occurs. We have found that VIPP1 does not interact with either components of the cpTat translocon or with the transport substrates. It also does not appear to increase the protonmotive driving force utilized by this transport pathway. Instead, VIPP1 appears to remodel the thylakoid membrane, establishing more grana at the expense of stromal membranes, and decreasing the membrane area from which cpTat substrates can be captured in non-productive locations.

We have also successfully transformed plants with pH-responsive GFP variants targeted to the chloroplast stroma and thylakoid lumen. Preliminary experiments with the latter constructs demonstrate that we can monitor pH changes in the lumen of isolated thylakoids in response to illumination via the GFP fluorescence signal. We have also observed this pH change in living tissue by confocal microscopy. We are now working to develop this new tool to inform us about the magnitude of the protonmotive force that drives protein targeting on the cpTat pathway and photophosphorylation.

Mechanism and Significance of Protein Maturation and Targeting in the Biogenesis of Photosynthetic Compartments

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Thylakoidal processing peptidase (TPP) is responsible for removing amino-terminal thylakoid-transfer signals from several proteins including oxygen evolving complex (OEC) subunits, cytochrome f and plastocyanin in the thylakoid lumen. There are three TPP homologs encoded in the nucleus of the model plant Arabidopsis thaliana, called plastidic type I signal peptidases 1, 2A and 2B (Plsp1, 2A and 2B). Our phylogenetic analysis revealed that TPP may have originated before the endosymbiotic event. The results also indicated that duplication leading to the two groups (Plsp1 and Plsp2A/2B) predates the gymnosperm-angiosperm divergence, and the separation of Plsp2A and Plsp2B occurred after the Malvaceae-Brassicaceae diversification.

Our biochemical and molecular genetic studies showed that Plsp1 was necessary for processing two OEC subunits and plastocyanin in thylakoids, and the protein import channel Toc75 in the chloroplast envelope in vivo. The lack of Plsp1 resulted in seedling lethality, apparently due to disruption of proper thylakoid development. Accumulation of unprocessed forms of Toc75 alone did not cause such a phenotypic defect. This result suggests that maturation of luminal proteins is necessary for thylakoid development. Results of expression profiling and genetic complementation assays suggest that Plsp1 and Plsp2A/2B play distinct roles and that neither of the Plsp2 isoforms is necessary for proper thylakoid development in photosynthetic tissues. We also discovered that Plsp1 forms a stable complex with PGRL1, a protein that was previously shown to be involved in modulating cyclic electron transport.

We are currently using molecular genetic and biochemical assays to address the following three questions: (1) How is Plsp1 targeted to thylakoids? (2) What is the physiological significance of the complex formation of Plsp1 with PGRL1? (3) What is the significance of lumen protein maturation for thylakoid development?

Photoreceptor Regulation and Optimization of Energy Harvesting in Nostoc Punctiforme

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Funding:	$1,000,000

BACKGROUND AND OBJECTIVES

Cyanobacteria are among the most versatile groups of photosynthetic organisms, capable of photosynthesis (with oxygen production) and nitrogen fixation (with hydrogen production). Like plants, cyanobacteria harvest solar energy and accumulate biomass (e.g., for biofuels such as biodiesel). While energy production by plants requires extensive use of nitrogen fertilizers and competes with food production for arable land, energy production by cyanobacteria allows growth in liquid culture without a need for fertilizers or arable land. However, cyanobacteria have not evolved to maximize energy production for our convenience, so it will be necessary to engineer them for more efficiency. Using the color or intensity of light to regulate gene expression offers a convenient, inexpensive toolkit for such engineering. Through characterization of photosensory proteins of the cyanobacterium *Nostoc punctiforme,* we are developing such a toolkit. *N. punctiforme* has a rich complement of such sensors, but it also forms symbiotic associations with plants via formation of specialized cell types called hormogonia. Such associations reduce the need for nitrogen fertilizers in plants with cyanobacterial symbionts. The specific objectives of our studies are to characterize all of the bilin-based photosensors in in this organism (a parts list), improve our understanding of how they work (the user manual), and use them to construct synthetic photosensory circuits for gene expression (the toolkit). Our investigations seek to examine how these proteins function, to elucidate the biological processes that they regulate, and to develop modular systems for light-regulated gene expression.

RESEARCH PROGRESS

During the funding period to date, our consortium has successfully cloned, expressed and purified 41 putative photosensory domains of the bilin-based photosensors from *N. punctiforme,* including 40 previously uncharacterized proteins. This parts list allows complete coverage of the entire visible spectrum and even the near-UV. Our studies have identified an astonishing variety of previously unknown photocycles and provide several candidates for structural and spectroscopic studies. Ultrafast spectroscopy has shown that one of these proteins, despite a nearly identical primary photochemistry to 'typical' phytochrome photosensors, possesses a quantum yield that is twice as high as any previously determined. Genetic approaches also have established a direct role for a specific photosensor in hormogonia phototaxis. Such insight should facilitate approaches to engineer symbiotic associations with crop plant species, reducing the amount of nitrogen fertilizer needed for a given plant yield.

Membrane Bioenergetics of Salt Tolerant Organisms

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Funding: $200,000

Ion pumps are devices that utilize chemical or photochemical reactions to generate and maintain chemical and electrical gradients for ions across biological membranes. Understanding how they couple a driving reaction to the translocation of an ion across the membrane is the main question of membrane bioenergetics. The potential benefits from better understanding biological energy conversion are vast as they include gains in biomass production, where even small increases in efficiency can have major economic impact. We initiate new work on the novel retinal-carotenoid proteins, xanthorhodopsin and gloeobacter rhodopsin. We had discovered that these, and several other related proteins, are light-driven proton pumps like bacteriorhodopsin, but contain a second chromophore, a carotenoid, which functions as a light-harvesting antenna. Our intent is to define the interactions of the retinal and the carotenoid in the proton transport cycle. The goals include study of the excited-state energy transfer to the retinal, the structural and functional consequences of the presence of the carotenoid in the protein, and the use of the carotenoid as a reporter molecule for the molecular events in the photoreaction cycle. The methods we will use are static and time-resolved visible and infrared spectroscopy, site-specific mutations, and continuation of the x-ray crystallography by which we had identified the location of the chromophores in xanthorhodopsin.

Molecular Genetic Dissection of Chloroplast Iron Homeostasis

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Iron nutrition limits life because of poor bioavailability. Photosynthesis on land and in the ocean occurs in an iron-deficient environment, yet our understanding of photosynthetic metabolism is based in a nutrient-supplemented laboratory situation. Recent studies have contributed to the appreciation of the photosynthetic apparatus as a dynamic entity whose composition, operation and output is tightly connected to resource availability. Technological advances have made it possible to monitor these properties, especially in microbial reference organisms where nutrient manipulation is facilitated. In Chlamydomonas reinhardtii, a eukaryotic chlorophyte alga, we have established four “stages” of iron nutrition – operationally defined on the basis of phenotype with respect to expression of iron assimilation pathways and light energy utilization. The long-term goal of this project is the discovery of mechanisms governing the iron-nutrition dependent programming of chloroplast metabolism in this reference organism. In the present project period, our immediate goals are to (1) undertake functional analysis of iron-nutrition responsive genes to distinguish functions in iron-sensing, photosynthesis, non-photochemical quenching, iron uptake/distribution or anti-oxidant responses from phenotypic analysis of under- or over-expressing strains; (2) identify iron-response elements on MSD3 and MDAR1 by mutational analysis of reporter constructs; and (3) continue ongoing transcriptome profiling and supplement the studies with proteome and metabolite profiles. The pathways in Chlamydomonas are representative either of those in land plants (e.g., NRAMPs and IRTs) or of those in phytoplankton (e.g., chloroplast MnSOD). Therefore, the work is broadly relevant and will lead to a better understanding of energy production and utilization in an iron-deficient environment. Our previous contributions have led to the development of biomarkers for assessing iron nutrition status in algae and has potential for contributing to metabolic flux engineering through manipulation of expression of individual ferredoxins.

FTIR Studies of Photosynthetic Oxygen Production

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Funding:	$160,000

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 carefully choreographing the proton and electron transfer reactions associated with water oxidation and by carefully managing both substrate (water) access and proton egress. The project's primary goal is to identify the amino acid residues that are responsible for this control and to determine the role of each. This information is crucial to understanding the mechanism of O_2 production in Photosystem II and will complement information that is being obtained from X-ray crystallography. The project's primary investigative tool is infrared (IR) spectroscopy. The project's primary aims are to identify and further delineate the dominant water access and proton egress pathways that link the Mn_4Ca cluster 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. Both FTIR difference spectroscopy and time-resolved IR spectroscopy are being conducted with mutant Photosystem II core complexes representing residues identified crystallographically or computationally as either potentially participating in networks of hydrogen bonds or potentially serving as catalytic bases. Identifying these residues and further delineating the networks of hydrogen bonds that form water access and proton egress channels will improve our understanding of the dynamic mechanism of water oxidation by the Mn_4Ca catalyst in PSII and will provide insight into the design of new generations of synthetic catalysts that convert sunlight into useful forms of storable energy.

Function of the Arabidopsis T1R1/AFB Auxin Receptors in Growth and Development

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During the last year, our focus has been in two areas.

(1) Function of the auxin co-receptor proteins AFB4 and AFB5. The AFB4 and AFB5 proteins are part of a six-member group of F-box proteins in Arabidospis. The other four members were previously shown to function as auxin co-receptors. During the last year we confirmed that AFB4 and AFB5 also bind auxin in the presence of a member of the Aux/IAA family of proteins. Biochemical studies demonstrated that AFB5 binds specifically to the auxinic herbicide picloram, and is the principle target of this herbicide. Further, we completed a genetic analysis of these proteins and showed that AFB4 has a particularly important role in seedling growth. Surprisingly, and unlike the other members of the family, AFB4 acts as a negative regulator of auxin signaling. Mutant afb4 plants are hypersensitive to auxin and as a consequence have a taller hypocotyl and petioles. The basis for this effect is under investigation.

(2) Temperature regulated seedling growth. We and others had previously shown that elevated temperature results in an increase in seedling growth and that this effect is dependent on auxin. During the last year we have initiated a project to investigate the role of auxin in this response. To determine which genes are involved in this response, we are performing RNAseq studies on hypocotyls and cotyledons at time intervals after a shift to elevated temperature. At present we are collecting the material required for this experiment. We have also performed a screen of mutants deficient in aspects of auxin signaling and homeostasis to identify which of these genes are important for the temperature response. Our results indicate that each of the TIR1/AFB proteins are involved but that AFB4 has a particularly important role. In addition, stabilization of the Aux/AA protein IAA7, completely inhibits the response, indicating that this co-receptor and transcriptional repressor is particularly important.

Integration of Sugar Transport, Metabolism and Sensing In Arabidopsis: Optimizing Energy Efficiency in Plants- Evaluating and Targeting Leaks

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The efficiency of plants to harvest the sun’s energy is essential for both crop and feedstock productivity. Don Ort and Steve Long outlined major sites in the mechanisms used for energy capture, conversion, and storage plant that require optimization to increase energy efficiency. These include, e.g., plant architecture for optimized light harvesting, cold tolerance to expand the annual period of light conversion, and the efficiency of the Calvin cycle. Principal targets for optimization are the regulatory networks that controls carbon partitioning and allocation. Another important aspect that is frequently overlooked is the loss of significant portions of photosynthate by wild and cultivated plant species to the soil/rhizosphere. Secretion is a significant drain regarding the overall energy status, with 1.5 t ha-1 a-1 or up to 30% of the net CO_2 assimilation. It has been speculated that secreted carbohydrates serve attraction and feeding of beneficial microorganisms in the rhizosphere. It has however so far not been possible to test this hypothesis, since the proteins involved in sugar efflux have not been identified, nor are mutants available. To identify the missing parts and for decryption of the biological circuits we need novel diagnostic tools that, analogous to oscilloscopes in electrical engineering of circuit boards, allow us to quantify fluxes for example by monitoring intermediates. Such probes can provide crucial information on systems properties such as metabolic impedance.

To measure steady state metabolite levels with minimal invasive methods, and to develop impedance measurements in vivo, we constructed a set of probes, namely Förster Resonance Energy Transfer (FRET) nanosensors. These probes, analogous to electrodes attached to an oscilloscope, can monitor metabolic impedance of a biological system at specific sites. The probes monitor the concentration of a specific metabolite with high temporal resolution and, since encoded genetically, can be targeted to specific cells or even specific cellular compartments and thus obtain measurements with cellular and subcellular resolution. The probes can be used to compare mutants or genetic variants and thus provide insights into the in vivo role of the respective components. Analysis can be performed in medium to high throughput allowing for systematic identification of missing components in mutant collections. Here, glucose, sucrose, and ATP FRET sensors will be deployed to (1) identify missing steps in transport, specifically carbon sequestration, and (2) systematically identify the signaling networks that control the roots energy status. The use of these FRET sensors in a mammalian expression system allowed us to identify a novel class of sugar effluxers that share functional features with the transport activities detected using the FRET sensors in plant roots. The aim of this project will be to identify and characterize the family members responsible for sugar efflux from roots, 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. In parallel, we will carry out a comprehensive analysis of sugar efflux from roots. Both aims will be achieved by combining radiotracer studies, metabolomics, as well as biochemical and biophysical tools such as surface-displayed FRET sensors and FRET biosensors to systematically define the mechanism of glucose efflux. A second aim is to develop plants in which the energy status can be directly quantified using FRET sensors for ATP. This set of approaches will help us to determine (1) the role of glucose efflux from roots and (2) whether it is feasible to reduce energy losses from roots and to restrict the resulting CO_2 emissions from soils. Moreover, we will establish new technologies that will be valuable for addressing important energy relevant questions in plants. To this end, we successfully identified a novel class of sugar transporters using the FRET sensors, named SWEETs. This novel class of sugar transporters has properties that match the ones we described in Arabidopsis roots. We also developed a screening system to analyze mutant plants. Interestingly, the SWEETs appear to be involved in plant pathogen interactions, and mutation of the plant genes leads to pathogen resistance.

Studies of Structure and Dynamics of Light Harvesting Complex 1 of R. Sphaeroides by Solid State NMR

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Light harvesting systems of natural photosynthetic membranes provide benchmarks for the efficient collection, storage, and directional transfer of energy from visible and near-visible photons. These systems exhibit novel physical-chemical phenomena of direct relevance to function, for example the fascinating but still unfolding story of the relatively long lived multi-chromophore coherences and their role in optimizing efficiency of energy transfer. One system of particular interest is light harvesting complex I (LH1 or B875) of purple nonsulphur bacteria, the immediate energy donor to the bacterial reaction center. Studies of anoxygenic prokaryotic systems, the purple nonsulphur bacteria, have contributed the key cornerstones towards understanding photosynthesis, the fundamental origin of bioavailable energy. There are a number of compelling reasons to understand this system, but nevertheless its structure remains poorly characterized. An 8.5 A resolution projection map observed by electron microscopy was reported for LH1 of Rs. Rubrum, and the crystal structure of the LH1-RC complex from Rps. palustris has been characterized by X-ray diffraction and resolved to 4.8 Å. At this resolution, the electron density map provides some important structural information, such as the positions and angles of the helices. The data show a reaction center surrounded by an incomplete LH1 ring containing 15 pairs of transmembrane aß subunit pairs arranged in an elliptical fashion. Molecularly detailed structural information, such as positions of pigments (carotenoids and bacteriochlorophylls), and conformations of key sidechains, could not be derived. Higher resolution structural information will be very important for advancing understanding of LH1. Moreover, conformational dynamical aspects of this complex are at the heart of its function. Solid state NMR studies will enrich our understanding of the conformational dynamics and the relation to function, both optimization of energy transfer and conformational control of quenching phenomena.

Using solid state NMR spectra, 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 predicted 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 offers a wonderful opportunity to do so.

Because in our initial exploratory experiments, the preparations had some minor degradation in the course of the NMR experiment, we recently validated the result under more native-like conditions. We established a collaboration with Richard Cogdell of the University of Glascow to compare LH1 complexes from Rhodobacter Paulstris and Acidophila to those from Spheroides. This comparison will allow us to see if the conformational plasticity is a general feature. We have tested the expression in appropriate isotopic media, scaled up the preparation, and are in the process of systematically varying the conditions for reconstitution into artificial membranes. This collaboration has also been important in connecting our solid state NMR results with the exciting single molecule optical studies.

Our next objective is to determine the three dimensional structure of the complex. For this objective it is essential to have the protein NMR resonances as well dispersed as possible. Our spectra from

Rhodobacter spheroids are very congested, and it is going to be difficult to interpret the tertiary contact information. The biochemical properties of Rhodobacter sphaeroides LH1 are suggestive of a less stable complex, which is possibly associated with the poor spectral resolution in comparison with other intrinsic membrane proteins. Therefore the collaboration with Cogdell is crucial in allowing us to investigate whether we can achieve better dispersion in the protein peaks form one of these organisms where the complex appears to be more stable. This is an important first goal towards the three-dimensional structure determination.

Another major objective of the proposal was the characterization of the fast conformational dynamics of the chromophores and protein functional groups, of possible relevance with respect to dissipative optical processes and heterogeneity in the complex. During this year we established and tested methods for dynamic characterization of the protein. Ms. Kuo-yin Huang has a manuscript regarding a new method using of 2H or deuterium NMR of extensively isotopically triply enriched (15N, 13C, 2H) 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, and additionally the 2H – 13C optimal magnetization transfer conditions can be independently used to answer the same question. The methods have been applied to model systems and to a small protein, and cross-validated against other strategies to obtain order parameters. Our immediate goal now is to utilize these methods on LH1, to measure the dynamical disorder as a function of temperature.

Chloroplast Dynamics and Photosynthetic Efficiency

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The goal of our project is to investigate the mechanism by which chloroplasts position themselves to maximize solar energy utilization 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 light that can cause photodamage. Chloroplast location is also important to facilitate exchange of metabolites between cells and with other organelles. Under limiting light, chloroplasts move to a periclinal position, perpendicular to the incident light (the accumulation response), where the surface area for light absorption can be maximized. Under potentially damaging light, chloroplasts move to anticlinal positions (the avoidance response) where many chloroplasts can be shielded from the light.

In plants, myosin XIs are responsible for motility of a variety of intracellular organelle cargo. We have investigated the role of the 13-member myosin XI family in chloroplast movement and positioning by labeling putative myosin tail cargo-binding domains with yellow fluorescent protein (YFP). Transient expression of 24 different YFP-labeled domains resulted in labeling of peroxisomes, mitochondria, endocytic vesicles, plastids and stromules, endoplasmic reticulum, nuclear envelope, Golgi bodies, and the plasma membrane, depending on the particular myosin XI domain. Some YFP-domain fusions labeled multiple organelles. The same organelle was labeled by YFP fusions to different myosin XIs, although only one myosin XI YFP domain fusion labeled chloroplasts.

A photometer with computer interface was devised in order to measure transmittance of light through leaves, which increases during the avoidance response and decreases during the accumulation response. Two different double myosin XI insertional mutants exhibited abnormal chloroplast movement in response to light. Leaves from plants undergoing virus-induced gene silencing of multiple myosins also exhibited reduced accumulation and avoidance responses.

In summary, three experimental approaches implicate myosin XI proteins in proper localization of chloroplasts to harvest light energy, to protect against photodamage, and to interact with other subcellular compartments.

Studies on Cytochrome bo3 from E. coli

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OVERALL RESEARCH GOALS

Cytochrome bo3 is a member of the superfamily of heme-copper oxidoreductases, which include the proton-pumping respiratory oxygen reductases that are present in most aerobic bacteria as well as in the eukaryotic mitochondria. The major aim of this grant is to investigate the structure and catalytic mechanism of the cytochrome bo3 ubiquinol oxidase from E. coli. This enzyme catalyzes the two-electron oxidation of ubiquinol-8 within the cytoplasmic membrane of E. coli and the four-electron reduction of O_2 to water. The considerable free energy available from this reaction is used to generate a proton motive force across the bilayer. For each turnover of the enzyme, 8 charges are translocated across the membrane, resulting in a transmembrane electrical potential. The reaction catalyzed by the enzyme is as follows.

The catalytic chemistry takes place at an active site containing a high-spin heme (heme o3) and a nearby copper (CuB). Our major biophysical tools are pulsed EPR, done in collaboration with Dr. Sergei Dikanov, and solid state NMR, done with Dr. Chad Rienstra.

Our goals include determining (a) the detailed nature of the hydrogen bonding between the protein and semiquinone radical, and the functional significance of the manner in which the semiquinone is stabilized by the protein; (b) the location of the tyrosyl radical that is generated during the cleavage of the O-O bond during the catalytic cycle; and (c) the detailed structural information on critical residues at the active site and within proton-input channels by using solid state NMR.

Radicals are generated in different steps of the mechanism.

(1) The oxidation of each ubiquinol molecule occurs in two steps, with the one-electron reduced semiquinone species generated as an intermediate. The semiquinone species can be stabilized and provides a probe to examine the protein environment around the semiquinone by pulsed EPR methods.

(2) The mechanism of the heme-copper oxygen reductases is proposed to require electron transfer from an active-site tyrosine (Y288 in cyt bo3) during the cleavage of the O-O bond. This tyrosine is always

cross-linked to a histidine which is one of the ligands to CuB. Reduction of the active site heme iron and copper can yield only 3 of the four electrons needed for O-O bond cleavage to give the known products.

Efforts to trap the neutral tyrosine radical and directly observe it have not been successful, possibly due to electronic coupling to the paramagnetic metals and/or due to a low yield during the transient reaction. We are placing non-natural amino acids in place of the active-site tyrosine to attempt to stabilize and observe the tyrosyl free radical.

SIGNIFICANT ACHIEVEMENTS (2009-2011)

To assist in both pulsed EPR and solid state NMR experiments, we increased the yield of recombinant enzyme to allow us to incorporate selectively labeled amino acids containing 13C, 15N or 2H. To facilitate this we generated a set of amino acid auxotrophs in the frequently used C43 expression strain, which is a derivative of E. coli BL21. These strains allow us to selectively label amino acids in the enzyme with high yield. We have also placed 13C both uniformly and in the methyl/methoxy groups of ubiquinone-8. These preparations have allowed us to obtain considerable information about the interaction of the protein amino acid residues with the unpaired electron spin of the semiquinone bound to cytochrome bo3. We have also demonstrated that selectively labeled cytochrome bo3 substantially simplifies the solid state NMR spectra and should allow us to make assignments of critical residues in the near future. In addition to work on cytochrome bo3, we have extended our studies to include the much smaller DsbB protein from E. coli, which is also a ubiquinol-binding protein, and the aa3-600 menaquinol oxidase from B. subtilis, which is a homologue of cytochrome bo3 which utilizes menaquinol in place of ubiquinol as a substrate.

Regulation of Chloroplast Biogenesis: the Immutans Mutant of Arabidopsis

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Funding:	$170,000

Variegated plants provide insight into mechanisms of chloroplast biogenesis. The immutans (im) variegation mutant of Arabidopsis has green/white sectored leaves containing normal chloroplasts (green sectors) and non-functional plastids (white sectors). The white sectors accumulate the C40 carotenoid precursor, phytoene, indicating that im conditions a defect in the activity of phytoene desaturase, the enzyme that converts phytoene to zeta-carotene in the plastid. With DOE support, we isolated the IMMUTANS gene by positional cloning (in 1999) and discovered that it codes for a chloroplast membrane protein that shows similarity to alternative oxidase (AOX), an inner mitochondrial membrane protein that serves as a terminal oxidase in the alternative respiratory pathway. Our results suggested that IM acts as a terminal oxidase in a redox chain that is responsible for the desaturation reactions of carotenogenesis; in the absence of IM early in chloroplast biogenesis, colored carotenoids cannot be produced and the developing plastids become photooxidized. Presumably, normal appearing chloroplasts in the green sectors contain factors that are able to compensate for a lack of the IM protein.

Over the years it has become clear that the IM gene product (designated PTOX, for plastid terminal oxidase) is an important alternative electron sink in photosynthetic membranes. Our DOE supported research has shown that it plays a fundamental role in developing thylakoids as a modulator of excitation pressure (thylakoid redox poise), and that its ability to reduce excitation pressure affords a prominent means of photoprotection to the developing chloroplast. We have also found that PTOX does not act as a safety valve during steady state photosynthesis, at least in Arabidopsis, which raises questions concerning its role in mature leaves. However, the fact that PTOX acts as a terminal oxidase during chlororespiration and during the desaturation reactions of carotenogenesis point to roles of this protein in non-green plastids. We conclude that PTOX resides at the nexus of a number of biochemical pathways in plastid membranes that rely upon oxidation of the PQ pool. Knowledge of the function of this protein is thus crucial for a complete understanding of energy transduction during photosynthesis.

The first aim of our research is to gain insight into factors that interact with PTOX. We also wish to identify factors that are able to compensate for a lack of PTOX in the green sectors of im. These studies should provide information about the early events of chloroplast biogenesis and pathways of retrograde signaling that are important in establishing the photosynthetic apparatus. Secondly, we have found that activation tagged AOX2, when localized in the chloroplast, is able to suppress im, and thus a second aim of our research is to understand how chloroplast AOX2 functions in thylakoids, and how the photosynthetic membrane adapts to the presence of this protein. We predict that novel mechanisms of photosynthetic function and AOX regulation will be found. Thirdly, our studies have shown that mitochondrial AOX1a is markedly upregulated in im mutants during chloroplast biogenesis, perhaps as a way of reducing excitation pressure in the chloroplast. The third aim of our research is to test this hypothesis using transgenic AOX1 plants in an im background. These experiments should lend insight into mitochondrial-chloroplast communication.

The proposed experiments have direct relevance to the Photosynthetic Systems program of the Chemical Sciences, Geosciences and Biosciences Division of Energy Biosciences inasmuch as their goal is to gain fundamental knowledge of the molecular mechanisms that govern energy transduction in photosynthetic systems.

Excitation Energy Transfer in Natural Photosynthetic Complexes and Chlorophyll Trefoils: Hole-Burning and Single Complex/Trefoil Spectroscopic Studies

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The research in this program is related to energy-relevant sciences including studies on photosynthetic energy capture by bacteria and artificial arrays. The research is in line with the current interests of the Department of Energy (DOE). It is anticipated that our research will shed more light on the performance of solar conversion systems including natural and artificial systems. Spectral hole-burning (SHB) and single photosynthetic complex/trefoil spectroscopy will be used to study the excitonic structure and excitation energy transfer (EET) processes as they occur in Chlamydomonas reinhardtii (Chlamy) PSI and PSI-LHCI, CP47 from spinach Photosystem II (PSII), and different chlorophyll (Chl) trefoils. To accomplish this goal we will use more sensitive readout techniques in SHB to study bulk/single photosynthetic complexes and Chl trefoils embedded in solid matrices at low temperature. Experimentally determined parameters will allow for better modeling of excitonic structure, low-energy states, and EET dynamics at a quantitative level. Chl trefoils are of great interest, as they cover a wide range of the solar spectrum, show rapid transfer of energy and form self-assembling aggregates.

Our long-range goal is to improve understanding of the electronic properties of the cofactors and the EET processes in both CP47 and Chlamy PSI. The key objectives are to (1) identify chlorophylls (Chls) that contribute to the “low-energy traps” in CP47 and PSI, and (2) examine their function and the origin of their large spectral shifts, and improve modeling of PSI and CP47 absorption and hole-burned (HB) spectra. We will demonstrate that non-photochemical hole growth kinetics (HGK) determined with a suitably wide range of burn intensities can resolve excited Qy states with overlapping absorption bands in CP47 and PSI complexes. Findings will be compared with data obtained by zero-phonon-line action spectroscopy and hole widths. A model will be tested to help determine that the different kinetics of holes burned in the region of several overlapping low-energy bands can provide information on EET between directly excited Chls and their neighbours in Chlamy PSI and PSI-LHCI. Finally, excitonic modeling studies will be performed for various antenna complexes (e.g. CP47 complex) and Chl trefoils. The Chl trefoils are of great interest, since they represent linked donor-bridge-acceptor molecular systems in which efficient, nearly distance-independent, photoinduced charge separation occurs. We will compare SHB and single trefoil spectroscopy (STS) data with time domain results. It is of great interest to use the experimental data generated by SHB/STS along with excitonic calculations to provide more insight into the electronic structure of these Chl trefoils, where the bridge is a conjugated organic molecule analogous to natural carotenes that transfer charge over long distances. Our rationale is that a better understanding of the structure-function relationship of natural systems will facilitate the development of artificial photovoltaic devices

To accomplish the goals of this program a partnership and collaboration has been established between the National Renewable Energy Laboratory (NREL) in Denver and the Department of Chemistry at Kansas State University (KSU). Collaboration has also been established with Prof. M. Wasielewski (Northwestern University) to study the electronic structure of various Chl trefoil arrays and with Prof. P. Fromme (Arizona State University) to study PSI.

Protein - Chloride Interactions in Photosystem II

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OVERALL RESEARCH GOALS

Our overall research goals are (1) identification of factors that contribute to the assembly/stability of cyanobacterial PS II and elucidation of the functional mechanism of these factors, (2) identification of the binding domains for the PsbP and PsbQ proteins in higher plants and CyanoQ and CyanoP in cyanobacteria, and (3) identification of novel components required for optimal photoautotrophy.

PRINCIPAL ACHIEVEMENTS 2008-2011

Our most recent achievements have centered on four areas: (1) Numerous protein components are required for the assembly/stability of PS II. We have identified a novel, cyanobacterial-specific assembly factor for PS II in Synechocystis. The protein Sll0606 is absolutely required for PS II assembly beyond the CP43-less reaction center core complex. (2) In higher plants, the PsbP protein of PS II is the founding member of a large lumenally localized family of proteins. A subset of these components, the PPD-like proteins, has not been well studied. We have examined Arabidopsis mutants (T-DNA and RNAi) lacking the PPD5 and PPD1 components. Mutants lacking the PPD5 protein exhibit a range of developmental defects consistent with a lesion in strigolactone biosynthesis and/or sensing. Mutants producing varying amounts of the PPD1 protein exhibit a variegated phenotype, the severity of which appears to correlate with the amount of accumulated PPD1 protein. (3) Numerous studies have used computational methods in an attempt to identify putative oxygen and water channels in PS II. We hypothesized that amino acid residue in contact with oxygen channels would be particularly prone to oxidative modification. Using Fourier-Transform mass spectrometry coupled with collision-induced dissociation, we have recently mapped the presence of oxidatively modified residues in spinach PS II and found that the only residues oxidatively modified and located within 20 Å of the Mn4CaO5 cluster are the CP43 residues 354E, 355T, 356M, 357R and 370R. This result suggests that these residues contribute to the oxygen egress channel from the photosystem.

Early Career - Thylakoid Assembly and Folded Protein Transport by the Tat Pathway

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OVERALL RESEARCH GOALS

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) determine the organization of the cpTat translocon; and (3) compare 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.

SIGNIFICANT ACHIEVEMENTS FY2011

Proteins destined for the thylakoid lumens 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 have undertaken topology studies of Tha4 via cysteine accessibility to membrane permeant and impermeant labels. N-terminal cysteine is not accessible to membrane impermeant labels but is accessible to membrane permeant labels. In addition, cysteine placed throughout the predicted amphipathic helix and carboxy tail region is susceptible to labelling with both kinds of labels. Taken together these data support a Nout-Cin 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.

Mechanisms of Chloroplast Division in Plants

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The proliferation of chloroplasts by binary fission during leaf development is essential for maximizing the efficiency of light harvesting and CO_2 fixation in plants. Chloroplast division is orchestrated by an elegant macromolecular machine comprising sub-complexes localized both inside and outside the organelle whose individual components must be properly assembled and disassembled and their activities coordinated across the two envelope membranes to constrict and sever the organelle. We have established a central role for the inner envelope chloroplast division protein ARC6 in coordinating the FtsZ ring inside the chloroplast with the ARC5/DRP5B (dynamin) ring outside the chloroplast via direct interaction with the outer envelope division protein PDV2. We propose to investigate the features required for ARC6-PDV2 interaction and test the hypothesis that phosphorylation of ARC6 regulates this interaction and hence ARC5/DRP5B recruitment. In addition, we have shown that a previously uncharacterized protein with homology to ARC6, called PARC6 (Paralogue of ARC6), functions downstream of ARC6 in plastid division. Genetic and preliminary biochemical analysis reveal a role for PARC6 both in regulating FtsZ assembly inside the organelle through interaction with the FtsZ-positioning factor ARC3, and in directing the outer envelope protein PDV1 to the chloroplast division site to promote ARC5/DRP5B recruitment and chloroplast constriction. In the proposed studies, we will carry out a series of biochemical and genetic analyses to dissect the role of PARC6 in plastid division by determining its localization and topological orientation, defining its interactions with ARC3, ARC6, PDV1 and other plastid division proteins, and studying its role in FtsZ assembly. These experiments will be critical for understanding the fundamental mechanisms underlying the activity of the chloroplast division complex in plants.

Regulation of Thylakoid Lipid Biosynthesis in Plants

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Funding:	$190,000

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, in particular of the photosynthetic membranes.

Galactoglycerolipids are the predominant lipids of photosynthetic membranes. Galactosyl transferases 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. Arabidopsis mutants disrupted in the import of lipids from the ER accumulate unusual oligogalactolipids and triacylglycerols for reasons currently not understood. Oligogalactolipid synthesis has been observed in isolated chloroplasts as well, and was attributed to the activation of a processive galactolipid:galactolipid galactosyl transferase (GGGT) associated with the chloroplast outer envelope. The Sensitive-to-Freezing 2 (SFR2) gene of Arabidopsis was shown to encode GGGT of Arabidopsis. Combining the sfr2 mutation with mutations disrupting lipid trafficking between the ER and the plastid determined that SFR2 is activated in the lipid trafficking mutants.

Oligogalactolipids also accumulate in the wild type following freezing and the sfr2 mutant lacking GGGT activity is freezing sensitive. Furthermore, excised mutant leaves do not produce oligogalactolipid in response to infiltration with different salts and small molecules. A new hypothesis was proposed linking GGGT activation during freezing to the prevention of membrane disruptions due to shrinkage of the organelle as water leaves the cell to form ice crystals in the apoplast. GGGT activity converts monogalactolipids to oligogalactolipids and diacylglycerols, which are converted to triacylglycerols. This process removes lipids from the chloroplast outer envelope membrane. It also changes the ratio of bilayer to non-bilayer forming lipids presumably preserving membrane intactness following chloroplast shrinkage. An in vitro assay for recombinant GGGT has been established to study its mechanism of regulation.

Different diacylglycerol pools at the inner and outer envelope membranes participate in the synthesis of chloroplast lipids. An approach specifically targeting bacterial diacylglycerol kinase to envelope membranes and the intermembrane space has been developed to interrogate different diacylglycerol pools. Transgenic plants targeting diacylglycerol kinase to the chloroplast envelope intermembrane space are most severely disrupted in growth, suggesting that an important diacylglycerol pool in the intermembrane space is being intercepted.

The Energy Budget of Steady State Photosynthesis

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Funding:	$168,000

In the first two years of our current project, we have addressed the mechanism of cyclic electron transfer around photosystem I (CEF1) which is important in balancing ATP/NADPH output and critical for responses of plants to their environments, the limitations to growth habitat and productivity, their responses to changing climate, as well as the engineering of improved photosynthetic efficiency or production of biofuels. We have isolated a new class of mutants in Arabidopsis and tobacco with substantially highly elevated CEF1. We then used these, together with new spectroscopic and metabolite profiling tools, to show that (1) the key step in higher plant CEF1 is likely catalyzed by the NDH complex (homologous to complex I of mitochondria), rather than other proposed enzymes; (2) the NDH complex likely pumps protons (like complex I); (3) CEF1 is activated by specific intermediates or signals, rather than simply slowing photosynthesis; and (4) other proposed processes (water-water cycle, the malate shunt or other CEF1 pathways) do not compensate for a loss of NDH under high CEF1 demand.

We request that the final year of the grant funding be transferred to the Kramer laboratory at Michigan State University, where we will complete the following sections of the proposed aims.

(1) Why do hcef mutants have increased CEF1? All but one hcef mutant has been cloned. We were unable to cross the remaining mutant, hcef4, into Ler. We will attempt to map the hcef4 mutant by a combination of rough mapping with crossing against a range of available ecotypes and deep sequencing using the MSU genomics core facility.

(2) Is increased CEF1 caused by elevated expression or altered regulation of CEF1 components? We observed a large increase in NDH expression in hcef1. We are extending these studies to all the other hcef mutants as well as the forward genetics mutants that we found showed high CEF1. In addition, we have initiated a preliminary chloroplast proteomics study of hcef1, hcef2 and hcef3 in collaboration with Dr. Mary Lipton at Pacific Northwest National Laboratory.

(3) Which metabolic pools can be regulators of CEF1? We feel our data rules out direct participation of measureable Calvin-Benson cycle metabolites in regulating CEF1. We are thus concentrating our efforts on H_2O_2, which we have strong evidence may be involved in regulating both expression and activation of NDH complex. Currently, we are writing a manuscript on these findings. To support this work, we are repeating key experiments exploring how generation of H_2O_2 affects the expression of CEF1-related proteins as well as the induction of CEF1 in a several mutant lines, including pgr5, gl1 (the background line for pgr5), and crr2-2.

(4) Do metabolites influence CEF1 directly or indirectly? Because of our findings about H_2O_2, this aim is now included as a sub-aim in aim 3.

(5) Which CEF1 pathways are activated in high CEF1 mutants? We have already published two papers related to this aim. To determine if NDH is the predominant route for CEF1, or if other can participate

under different conditions, we are crossing all of the high CEF1 mutants we have found against pgr5, crr2-2 and nda1. Results thus far show that in each case NDH is the major pathway for CEF1. When results are complete we will publish in a series of papers.

(6) Is PQR a proton pump? Our results strongly suggest that the PQR is a proton pump. We will work to further test this by comparing results from higher plants, in which PQR is likely NDH, and a proton pump, with those from Chlamydomonas, which lacks NDH but contains a type-2 NADPH-PQ oxidoreductase which cannot pump protons.

(7) Is elevated CEF1 activated by state transitions? Our results so far indicate that CEF1 is not regulated by state transitions. We are currently preparing a manuscript on these results.

Elucidation of Mito-Nuclear Interplay in Arabidopsis

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Previous funding from DOE-BES allowed the identification and cloning of the MUTS HOMOMLOG 1 (MSH1) gene in plants. Detailed study of this gene reveals that its protein is targeted to both mitochondria and chloroplasts, where it participates in maintaining genome stability. Consequently, manipulation of MSH1 expression might allow us to gain information about the phenotypic consequences of organellar perturbation in plants. During the course of this study, we have made two important discoveries. The first is that the most dramatic phenotypic changes that emerge in the msh1 mutant or RNAi suppression line are derived not from mitochondrial perturbation, but from chloroplast. These include altered gibberellic acid catabolism, producing dwarfing, altered auxin responses leading to changes in branching pattern, and altered vernalization, flowering time, stomatal density, maturation and stress responses. We observed these MSH1-derived developmental changes in MSH1 RNAi suppression lines of six different plant species. Secondly, we have learned that these programmed developmental changes are epigenetic, independent of the RNAi transgene, MSH1 expression and the original chloroplasts once the changes are induced. Our results provide the first evidence to suggest a link between organellar behavior and the epigenome, likely permitting future studies of plant behavior in response to environmental cues.

Role of the Rubisco Small Subunit

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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. Recently completed work has shown that a small-subunit L66F substitution at the interface between large and small subunits mimics the conformational dynamics of a large-subunit L290F substitution, and both mutant enzymes have decreases in CO_2/O_2 specificity. An L66G substitution, which introduces the smaller residue found in land-plant Rubisco, suppresses large-subunit L290F and improves the CO_2/O_2 specificity and carboxylation catalytic efficiency of the wild-type enzyme. In an attempt to determine whether the solvent channel may play a role in holoenzyme conformational changes that occur during catalysis, substitutions were made at Ile-58, which defines the narrowest diameter of the channel opening. Single substitutions had little or no effect. However, when three Trp residues were introduced in place of Ile-58 (introducing 12 Trp residues from four small subunits), CO_2/O_2 specificity and holoenzyme thermal stability were decreased. Similar results were obtained when chimeric small subunits were created with the short βA-βB loop and long carboxyl-terminal extension of the red-algal *Galdieria* small subunit. In *Galdieria*, carboxyl-terminal residues provide structural interactions at the opening of the solvent channel that are similar to those of the longer βA-βB loop in the *Chlamydomonas* small subunit.

Altogether, these results indicate that the small-subunit βA-βB loop must influence large-subunit catalysis by a global effect on Rubisco conformation or conformational dynamics, and may serve as a future target for engineering improvements in the enzyme. Ala-scanning mutagenesis of the most conserved small-subunit residues identified other interactions between large and small subunits that influence catalysis. Recent work has focused on Tyr-32, which shields the carboxyl-terminal end of large-subunit α-helix 8 from solvent. Y32A is the only mutant substitution outside of the βA-βB loop that affects CO_2/O_2 specificity. Y32A, Y32D, and Y32E substitutions decrease CO_2/O_2 specificity and holoenzyme thermal stability in vivo and in vitro, but Y32F and Y32R substitutions do not. It seems likely that either a phenolic ring or positive charge complements the partial negative charge at the carboxyl-terminal end of α-helix 8. This interaction may influence the position or amino-terminal charge of α-helix 8, which, in turn, may influence interactions between amino-terminal α-helix-8 residues and the carboxylation transition state. These results can explain how changes far from the active site affect catalytic efficiency.

Asparagine Synthetase Gene Regulatory Network and Plant Nitrogen Metabolism

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The goal of this DOE project is to model and alter metabolic regulatory networks affecting N-assimilation into the amino acid asparagine (Asn), a C- and N-efficient amino acid used to transport and store nitrogen in seeds. We previously showed that altering the transcription of ASN1, the major gene controlling Asn synthesis in Arabidopsis, effects dramatic increases in Asn in seed and increases seed N content. This technology is currently in field trials of corn and other crops to improve N-use efficiency. Using a combination of genetics, genomics, and systems biology tools we uncovered regulatory mechanisms operating at the level of chromatin regulation and transcriptional control that regulate a plant's metabolic network. These regulatory mechanisms coordinate ASN1 expression with a network of genes involved in C- and N-metabolism, photosynthesis, and energy production. Our goal is to study and modify these regulatory mechanisms with the aim of increasing C- and N-use efficiency in plants.

SIGNIFICANT ACHIEVEMENTS (2008 – 2011)

Approach: Using a combined genetic, genomic, and systems biology approach, we have uncovered the molecular components regulating Asn synthesis and metabolism in response to carbon (C), light (L) and nitrogen (N) signals. Using a positive genetic selection, Arabidopsis mutants impaired in C and L repression of an ASN1promoter::HPT2 transgene were isolated to identify the molecular components involved in the regulation of ASN1 in response to C and L signals. Transcriptome analysis of one C and L insensitive mutant, CLI186, uncovered a metabolic regulatory network that coordinates the regulation of genes involved in C and N metabolism, photosynthesis, and energy production. Map-based cloning revealed that CLI186 encodes a histone lysine methyltransferase involved in H3K4/K36 methylation that was previously associated with FLC, a repressor of flowering. We will test the hypothesis that the specific histone methyltransferase encoded by CLI186/EFS, poises a metabolic network of genes involved in C and N-metabolism for coordinated regulation with photosynthesis and energy production. We are using Chip-seq approaches to explore the role of chromatin modification in the coordination of this metabolic gene network in plants, as detailed below.

Plans for 2011-2012: We will use transgenics and site directed mutants of CLI186/EFS to test whether and how CLI186/EFS coordinates methylation of H3K4me3 (at promoters) and K36me2 (in gene body) in this metabolic regulatory network (Aim 1). We will also begin to explore the downstream TF networks that coordinate the reciprocal regulation of Asn synthesis (via ASN1) and Asn metabolism (via ANS1) with related processes including photosynthesis and energy (Aim 2). Additionally, we will expand our transcriptional studies to the level of N-metabolites to test whether mutants in structural and regulatory genes controlling Asn synthesis and/or metabolism affect flux of 15NO3- into Asn. We will also test whether Asn functions in N-signaling in vivo to regulate genes in this metabolic regulatory network (Aim 3).

Studies of Photosynthetic Reaction Centers and Biomimetic Systems

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Funding: $166,000

The goal is to establish a research program for fundamental studies of natural photosynthetic proteins and biomemetic systems, incorperating Monte Carlo simulations for calculations of pKas and electrochemical midpoints (Gunner, CCNY); quantum mechanics and QM/MM analysis (Batista, Yale Univ, USA); and large-scale molecular dynamics of photosynthetic reaction centers (Bruce, Brock Univ, Canada). Our efforts have been focused on reevaluating the structure of the Oxygen Evolving Complex (OEC) of Photosystem II (PSII) given the new X-ray crystal model, the mechanism of O-O bond formation the functional role played by Cl during water splitting), and the limits of the energy necessary to drive oxygenic photosynthesis.

REFINEMENT OF THE OEC STRUCTURE

The combination of experimental information from EXAFS and X-ray diffraction data and DFT QM/MM simulations allows for a significant level of structural refinement of the OEC structure. A refined quantum mechanics/molecular mechanics (QM/MM) model of the OEC Mn_4CaO_5 complex of photosystem II in the S1 Mn_4(IV,III,IV,III) state was developed from the new 1.9Å resolution X-ray diffraction model. The QM/MM model is consistent with high-resolution spectroscopic data, including polarized EXAFS of oriented single crystals. This refines the intermetallic distances within the Mn cluster and suggest that the x-ray model most likely corresponds to a mixture of oxidation states, including species more reduced than those observed in the catalytic cycle of water splitting.

MECHANISM OF O-O BOND FORMATION

The functional roles of carboxylate moieties contact with the OEC and substrate water molecules in the mechanism of O—O bond formation catalyzed by the OEC of PSII and by the biomimetic Mn-terpy complex is being explored by QM/MM simulations. Carboxylate groups directly attached to Mn centers are found to be non-innocent ligands in the reaction since they engage in charge transfer interactions that facilitate the activation of the catalytic complex through PCET leading to the water nucleophilic attack on the Mn-oxyl species during O-O bond formation.

CHLORIDE BINDING IN PHOTOSYSTEM II

Chloride is essential for photosynthetic water oxidation. MD and MC simulations show that chloride depletion induces formation of a salt bridge between D2-K317 and D1-D61, a structural motif that could suppress proton transfer to the lumen from the OEC. Chloride moves near D2-K317 and displaces D1-D61 in a position close to that found in the 1.9 Å resolution PSII X-ray crystal structure. In addition, chloride binding raises the D1-D61 pKa so that it may become a transient acceptor of protons from the OEC and potentially transfer protons to the lumen.

LIMITS ON PHOTON ENERGY FOR OXYGEN EVOLUTION IN PSII

The cyanobacterium Acaryochloris marina uses chlorophyll d to carry out oxygenic photosynthesis. PSII absorbance now peaks at ˜720 nm rather than 680 in T. Elongatus representing a loss of ˜90 meV of the available energy. Measurements of the energy-storage efficiency of the photosynthetic light reactions by photoacoustic spectroscopy in A. marina whole cells showed it is comparable to, or higher, than that in typical, chlorophyll a-utilizing oxygenic species. MC simulations show a ˜40 meV loss in oxidizing potential of P+ and ˜50 meV loss of the P* reducing power. Thus, the protein loses a small amount of energy in both directions and thus maintains efficient quantum yield.

Amidase-Mediated Modulation of N-Acylethanolamine (NAE) Signaling Pathway in Plants

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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. The proposed research fits well within the stated mission of Physical Biosciences to support "fundamental understanding of the complex processes that convert and store energy in living systems [including] studies that investigate the mechanisms by which energy transduction systems are assembled and maintained." The basic processes that govern the critical stages of seedling establishment have direct impact on the assembly of photosynthetic energy conversion systems in essentially all higher plants. Here we propose to continue our efforts to understand the role of NAE metabolism in the regulation of seed and seedling development using a combination of biochemical and molecular tools established by prior DOE-supported research efforts. Our main hypothesis is that fatty acid amide hydrolase (FAAH), a member of the amidase superfamily of proteins, influences plant growth by both its catalytic hydrolysis of endogenous bioactive NAEs and through its interaction with proteins involved in RNA metabolism. Evidence suggests that these bifurcating actions of FAAH are central to modulating ABI3 transcript levels, a key transcription factor regulating the embryo-to-seedling transition, and thereby provides a connection between NAE metabolism and ABA signaling in the regulation of seedling growth. Three specific aims are proposed: (1) Delineate the mechanisms by which FAAH1 interacts with proteins to modulate ABI3 transcript levels independent of its catalytic activity toward NAEs. (2) Attribute specific effects of polyunsaturated NAE species on aspects of seedling growth—Ca^{2+} signaling in root cells, root elongation, and chloroplast development in cotyledons. (3) Examine the impact of $FAAH_2$ on the interaction between ABA signaling and NAE metabolism.

Production of Biofuels and Value-Added Products via Solar and Chemical Energy Driven Bioconversions

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In Rhodobacter sphaeroides, CbbR and RegA (PrrA) are transcriptional regulators of the cbbI and cbbII (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 cbbI 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 cbbI promoter enhanced by RegA. Conversely, RegA interactions with CbbR did not require RegA to bind the cbbI promoter. RegA itself formed incrementally larger multimeric complexes with DNA as the concentration of RegA increased. The presence of RegA binding sites 1, 2 and 3 promoted interactions at significantly lower concentrations of RegA than when RegA binding site 3 is not present in the cbbI promoter. These studies support the premise that both CbbR and RegA are necessary for optimal transcription of the cbbI operon genes of R. sphaeroides. A model depicting how the CbbR-RegA complex might interact with the transcription machinery of the cell has been developed.

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. The bacterial two hybrid system established a specific interaction between CbbR and CbbRR1 (response regulator 1 of the CbbRRS system), confirmed in vitro by chemical crosslinking. In addition, both response regulators (CbbRR1 and CbbRR2) played distinct roles in influencing the CbbR-cbbLS promoter interactions in gel mobility shift assays. CbbRR1 increased the binding affinity of CbbR at the cbbI promoter 3-5 fold while CbbRR2 appeared to stabilize CbbR binding. Specific interactions were further supported by surface plasmon resonance (SPR) analyses. In total, the results suggested that both response regulators, with no discernible DNA binding domains, must interact with CbbR to influence cbbLS expression. Thus the CbbRRS system provides an additional level of transcriptional control beyond CbbR alone, and appears to be significant for potentially fine tuning cbbLS expression in Rps. palustris.

Unraveling Genetic Regulatory Circuits Integrating the Light and Dark Reactions of Oxygenic Photosynthesis

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The overall objective is to better understand the cyanobacterial high affinity inorganic carbon concentrating mechanism (CCM) in terms of its integration with the light and dark reactions of oxygenic photosynthesis. During the first funding period, the control of the transcription of the inducible high affinity CCM genes was found to be modulated by key photosynthetic metabolites, including NADP+, which serve to modify the DNA binding activity of regulatory proteins. The work will continue testing the general hypothesis that the genetic integration of the CCM with the light and dark reactions is achieved mainly through physiological interactions involving metabolic intermediates that connect the different photosynthetic processes.

The proposed effort has two broad aims:

(1) Build on the findings of the previous funding period and test a working model for the CCM regulatory that involves control by key photosynthetic metabolites, including NADP+, which serve to modify the DNA binding activity of regulatory proteins. Now, we will test predictions regarding the changes in the cytoplasmic concentrations of these metabolites under various conditions that influence the expression of the CCM. The experiments will employ biophysical and biochemical analyses that are designed to shed light on the dynamic interactions between photosynthetic metabolism and the adaptive mechanisms controlling gene expression under changing environmental conditions.

(2) Engineer the cyanobacterial CCM in various ways to better understand its functional operation and develop tools for re-constructing chimeric versions of the CCM. This aim will involve the re-creation of an existing strain that completely lacks a CCM, but in a new genetic configuration (marker-less in terms of antibiotics) that will be highly valuable due to its projected versatility for this project and beyond. The central engineering aim, is to create a recipient strain that will have very broad utility for a variety of studies starting with the redox-CCM questions posed here to future studies that would benefit from an easy to use positive molecular genetic selection environment to drive more efficient forms of the CCM and even RubisCO. This strain will then be used to address questions on the regulation and structure of two of the operons—sbtA/B and ndhF3/ndhD3/cupA/cupS—using a chimeric approach involving other cyanobacterial species.

RATIONALE

The acquisition of inorganic carbon very often limits photosynthetic performance in natural systems and this limitation is likely to be even more acute in engineered systems that may have proportionally higher demands for inorganic carbon relative to other nutrients. Additional significance derives from the emerging picture that the cyanobacterial CCM is a actually a remarkable example of evolutionary re-configuration of redox-driven energy conversion system to a redox-driven nutrient acquisition system that involves a ion gradient driven bicarbonate symports and CO_2 hydration mechanisms all of which remain only superficially understood. Not only does this situation provide a rich field of potentially fascinating and practically useful structure-function information, but also its modularity may prove to be a good model for understanding the applications and limits of engineering chimeric regulatory and enzymatic systems. The work provides excellent and engaging multidisciplinary training opportunities for a postdoctoral fellow and students.

Analysis of Anther Cell Differentiation

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Plant reproduction and yield depend on normal anther development. We have used Arabidopsis as a model system to study the genetic control of anther cell differentiation. Building on our previous work with the SPL, EMS1, and DYT1 genes, we have during the current funding period performed transcriptomic comparison between wild-type and dyt1 mutant anthers, and found about 900 genes that are differentially expressed, including known anther regulatory genes MYB35, AMS, MYB103, and MS1. We have further demonstrated that the DYT1 protein can bind to the promoter region of MS1 and other sequences containing a G-box. These results support the idea that DYT1 is a key transcriptional regulator for normal anther cell differentiation. We have further carried out anther microarray analysis of the ams mutant and identified several hundred genes with altered expression. Careful analysis of these results and previous microarray data for spl and ems1 mutant anthers revealed various patterns of gene expression, suggesting complex gene regulatory interactions. We have prepared a manuscript describing some of these results. During our analysis, we have suggestive evidence that the dyt1 and ams mutants might respond to environmental signals and modulate reproduction. To obtained clues about the effect of environment on reproductive development, we have initiated experiments to characterize anther development and other aspects of reproduction under conditions of reduced water, and obtained preliminary results on development and transcriptomes. These results provide new understanding of the control of plant reproduction, and may contribute to great biomass production.

Light Energy Transduction in Green Sulfur Bacteria

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Chlorophototrophs, chlorophyll-dependent phototrophs that synthesize bacteriochlorophylls (BChls) or chlorophylls (Chls) and reaction centers (RCs), perform the fundamental process that permits life to exist on Earth: the capture and conversion of light energy into chemical energy for the subsequent fixation of CO_2 into biomass. This proposal principally focuses on “green bacteria,” organisms that synthesize BChl c, d, or e and use these BChls to assemble chlorosomes, remarkably efficient light-harvesting organelles. Chlorosomes are protein-lipid enveloped sacs that can contain up to 250,000 BChl c, d or e molecules, and they enable green bacteria to harvest light at remarkably low irradiance levels. These bacteria are important primary producers in many anoxic environments, and they contribute significantly to the biogeochemical cycling of carbon, nitrogen, and sulfur on Earth. The long-term objectives of this research program are to understand the design principles of chlorosomes, i.e., their structure, function, and biogenesis. We also seek to understand the reaction centers (RCs) and electron transport chains that transduce absorbed light into chemical energy in these organisms. Chlorosomes are an important model system because the self-assembly properties of the BChls occurring in chlorosomes can be exploited in 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.

We are studying chlorosomes and RCs in organisms from very different environmental niches: Chlorobaculum tepidum, Cba. limnaeum and Cba. yellowstoneii, occur in anoxic, sulfide-rich environments. Cba. tepidum is a strictly anaerobic, moderately thermophilic, green sulfur bacterium (GSB) that has Type-1 RCs, a BChl a-binding FMO protein, and chlorosomes containing BChl a and c. Candidatus Chloracidobacterium thermophilum, is a newly discovered aerobe from the phylum Acidobacteria. It is the first aerobe described with chlorosomes, FMO and simple homodimeric Type-1 RCs. Ca. C. thermophilum is an abundant organism in the phototrophic microbial mat communities of alkaline hot springs, but many details about its photosynthetic apparatus are still lacking. We have recently made two unique and surprising discoveries about its RCs: they include a carotenoid-binding protein, and they are the first RCs that contain three Chls: Chl a, Mg-BChl a, and Zn-BChl a’. We recently discovered a second aerobic thermophile, Ca. Thermochlorobacter aerophilum, which is also an aerobic, photoheterotrophic; it belongs to phylum Chlorobi but is only distantly related to Cba. tepidum and other members of the Chlorobiales.

To investigate the ecophysiology and metabolic capabilities of green bacteria, we employ genome sequencing, comparative bioinformatics and genomics, genetics, biochemistry, biophysics, and structural biology approaches. The experimental studies in this proposal will extend our progress during the current funding period in several areas: (1) exploitation of the first genetic system in a BChl-e producing GSB, Cba. limnaeum, to study chlorosomes and the ecophysiology of BChl e-producing organisms; (2) characterization of the carotenoid binding protein and Type-1 RCs of the newly discovered chlorophototroph, Ca. C. thermophilum; (3) structural and spectroscopic studies on chlorosomes; (4) elucidation of the pathway for BChl e biosynthesis in Cba. limnaeum and carotenogenesis pathways; (5) cultivation and characterization of novel chlorophototrophs; and (6) genomics-enabled studies of chlorophototrophs in their natural habitats. Comparisons of the properties of chlorosomes and homodimeric Type-1 RCs of organisms inhabiting anoxic (Cba. tepdium and Cba. limnaeum) and oxic (Ca. C. thermophilum and T. aerophilum) environments should reveal important adaptations to these two very different niches and will provide new information about the evolution of photosynthesis as well as the design principles for artificial photosynthesis. We will exploit the ~50 chlorophototroph genomes that we have obtained in phylogenetic profiling, gene neighborhood analysis, and other comparative bioinformatics approaches to identify genes responsible for key biochemical processes in these remarkable, environmentally important microorganisms.

The Type I Homodimeric Reaction Center in Heliobacterium Modesticaldium

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The goal of our BES-funded program in Chemical Sciences, Geosciences and Biosciences is to understand the structure, function, and organization of the homodimeric Type I reaction center found in Heliobacterium modesticaldum. The overall idea is to 'jump start' the study of a simple Type I reaction center, so that with the acquisition of high-resolution X-ray crystal structures, mutagenesis techniques, biochemical protocols, and biophysical tools, structure/function studies can be carried out on a simplified photochemical reaction center that works at the reducing end of the biological redox scale. Our first goal is to determine the 3-dimensional structures of the heliobacterial reaction center core and the FA/FB-containing polypeptides. Here, we have extended the purification originally published for the HbRC by adding a second chromatography step and we have found that the stoichiometry of cofactors within the HbRC is 19±3 BChl g : 2 BChl g' : 2 81-OH-Chl aF : 1 4,4'-diaponeurosporene : 1.6 menaquinone (7:1 ratio of MQ-9:MQ-8). The resulting preparation has no contamination by cytochrome c553 and several ABC transporters, which were a problem with the previous preparation. We are actively engaged in crystallization of the HbRC from this preparation.

Our second goal is to determine whether the PshB1 and PshB2 polypeptides are true subunits of the heliobacterial reaction center, or whether they are the quasi-mobile acceptor proteins. The gene that codes for PshB, HM1_1462, is part of a predicted dicistronic operon that contains a second gene, named HM1_1461, which codes for a second ferredoxin-like protein with high sequence homology to PshB, including the two traditional [4Fe-4S] cluster binding motifs. RT-PCR results confirm that both genes are transcribed as a single transcript. We have cloned the HM1_1461 gene through PCR amplification of the H. modesticaldum chromosomal DNA and overexpressed the apoprotein in Escherichia coli. Reconstitution studies with inorganic reagents have shown that the holoprotein harbors ~8 iron and ~8 sulfide atoms in the form of two [4Fe-4S] clusters. Incubation of the reconstituted holoprotein with heliobacterial reaction center cores results in a charge-separated state characteristic of electron transfer past the FX cluster to the terminal [4Fe-4S] clusters FA and FB. These results suggest that the HM1_1461 product, which we have named PshBII, is capable of functioning in lieu of PshB (renamed PshBI) as an alternative terminal electron transfer protein. Thus, unlike PS I, to which PsaC is tightly bound, two loosely bound ferredoxins, PshBI and PshBII, interact with the heliobacterial reaction center.

Our third goal is to determine whether other ferredoxin-like proteins function as electron acceptors from FX. We had proposed earlier that PshBI and PshBII are quasi-mobile electron transfer proteins that, upon reduction, dissociate from the HbRC and reduce downstream metabolic partners. Using P800-FX cores devoid of PshBI and PshBII, we show that the iron-sulfur cluster FX directly reduces the souble redox protein flavodoxin without the involvement of PshBI and PshBII. The maximum rate of flavodoxin reduction occurs at pH 8.0 in the presence of 5 mM $MgCl_2$ and 20 mM NaCl with phenzine methosulfate as the electron donor to P800+. Increasing the ionic strength leads to a significant loss of activity, an effect reminiscent of the ionic strength-dependent loss of PshBI/PshBII from membranes and HbRCs. The reduction of flavodoxin is suppressed by the presence of PshBI or PshBII, an effect that can be explained on the basis of competition for the electron on FX. This is the first report of the FX cluster participating in forward electron transfer to a completely soluble redox protein in any Type I reaction center and implies that the membrane-embedded PshA homodimer should be capable of donating electrons directly to a variety of soluble redox partners in heliobacteria.

Membrane-Attached Electron Carriers in Photosynthesis and Respiration

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The long-term goals of our work are to define the nature, mechanism of function, and biogenesis of bacterial cytochromes (cyt) and cyt containing energy transduction complexes. Cyts are ubiquitous hemoproteins that are key electron carriers in energy and signal transduction pathways. These proteins are essential for cellular processes extending from the production of chemical energy (ATP) to the induction of cell death (apoptosis). We aim to contribute to a mechanistic understanding of the energy transduction pathways, including photosynthesis (Ps) and respiration (Res). We use the facultative phototrophic Rhodobacter (R.) species that provide excellent experimental models for these studies.

Our work started with the discovery of electron transport (ET) pathways that use the membrane-bound electron carrier cyt cy in R. capsulatus. Cyt cy carries electrons from the cyt bc1 to the photochemical reaction center in Ps-ET, or to the cyt c oxidase in Res-ET. Supported by this grant, we defined the rules governing efficient interactions between cyt cy and its partners, developed novel 'hard-wired' ET complexes, and studied their molecular organizations in membranes. At the same time, we also investigated the biogenesis of cyts c, which is the attachment of a covalent heme cofactor to an apocyt c (cyt c maturation, Ccm) to yield a mature holocyt c, and assembly of holocyts c into functional multi-subunit membrane complexes.

Understanding how cells make and maintain (maturation, assembly and repair) the cyts c is a fundamental process with major significance for efficient biological energy conversion, as cyts c are integral components of Ps- and Res-ET pathways. Our current efforts are focused on the Ccm process, which is found virtually in all living organisms, and the specific Ccm (System I) that we study occurs in bacteria, archaea, mitochondria of plants and red algae. Our previous work uncovered the R. capsulatus CcmI, CcmE, CcdA and DsbA-DsbB components, and contributed to our understanding how Ccm occurs and how the c-type cyt-containing multi-subunit cyt cbb3 complex is assembled. Ongoing work is focused on deciphering physical interactions between the apocyt c and heme as substrates, and CcmI, CcmH, CcmG and CcmHFI complex as chaperones and catalysts of Ccm. We believe that these studies are relevant to energy biosciences and their applications. They are of broad biological significance as the biogenesis components are part of major cellular functions, including protein translocation, extra-cytoplasmic protein folding and degradation, redox homeostasis, metal trafficking and insertion into proteins. Hence their understanding is of utmost importance for our mastery of photosynthetic and respiratory energy generating processes.

Novel Photoprotection Mechanisms in Closely Packed Photosynthetic Antenna Complexes and in Artificial Light-Harvesting (Bacterio)Chlorophyll Aggregate

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Bacteriochlorophyll (BChl) and chlorophyll (Chl) molecules play a major role in the process of photosynthesis. Surprisingly, monomeric (B)Chl molecules photo-degrade in a matter of minutes under sunlight due to efficient energy transfer from their excited triplet states to oxygen molecules and consequent formation of highly toxic singlet oxygen. It has been shown that in (B)Chl pigment-proteins of photosynthesis, a carotenoid is typically positioned near individual (B)Chl or antenna arrays, allowing rapid triplet energy transfer from (B)Chl to the carotenoid that prevents singlet oxygen formation. The latter mechanism has been believed to be universally utilized in all photosynthetic complexes. Our experiments revealed that an alternative very efficient intrinsic photoprotection mechanism functions in natural and in artificial complexes that contain strongly coupled (B)Chl arrays of pigments. This mechanism does not require the presence of carotenoids but still leads to ~1000 times increase in photostability of (B)Chls. Our work on chlorosomes and artificial complexes show that this extraordinary level of photoprotection is caused by lowering of the triplet state energy of (B)Chls below that of singlet oxygen in strongly coupled light harvesting complexes and appears to arise due to the formation of triplet excitons/excimers.

The main goal of this proposal is to thoroughly characterize the properties of triplet states in closely coupled natural and artificial systems and quantify the degree of photoprotection arising as a consequence of aggregation. It is expected that this novel photoprotection mechanism is universal and functions in all strongly coupled pigment-protein complexes, such as, for example, chlorosomes and Fenna-Matthew-Olson complexes. While there is extensive research on triplet excitons/eximers in molecular crystals, there has been no prior mention of triplet excitons/excimers in native and artificial photosynthetic systems and of their biological function in the literature.

The low photostability of artificial light-harvesting antennae remains one of the greatest challenges in their use for solar energy utilization that mimic the highly efficient photosynthetic processes. The intrinsic property of strongly coupled pigments to photoprotect themselves opens a new path in design of such artificial antennae that are not only extremely efficient in solar energy harvesting, but are also exceptionally stable. Our experiments show that artificial BChl aggregates, which can be synthesized through a simple self-assembly process, are not only extremely efficient light harvesters, but are also very stable under light due to the presence of this intrinsic photoprotection mechanism.

Regulation of Actin Filament Ends: The Role of Capping Proteins in Plant Growth and Lipid Signaling

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The cytoskeleton comprises a filamentous network that consumes enormous amounts of cellular energy to undergo constant rearrangements and to support a myriad of essential processes. In plants, actin filaments serve as dynamic “tracks” for the motility and positioning of organelles, including chloroplasts and Golgi, and guide secretory vesicles containing polysaccharides to the plasma membrane for cell wall assembly. The construction and turnover of these cellular highways is regulated by a myriad of actin-binding proteins. Our overall research goal is to understand and gain molecular control of the mechanisms that underpin actin filament turnover in plant cells. Here, we are investigating the properties and function of the heterodimeric actin capping protein from Arabidopsis (CP). The specific aims of this project include (1) characterizing the role of CP in actin stochastic dynamics, (2) dissecting synergies between CP and other cappers, and (3) understanding where CP is located in living cells and how it contributes to organelle function. This will be accomplished with a multifaceted attack that combines advanced imaging modalities applied to live cells, with biomimetic systems, and with reverse-genetic analyses in Arabidopsis.

Previously, we had characterized the biochemical and biophysical properties of the filament end-binding protein, AtCP. 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 as well as a simple reconstituted system for motility, was developed to describe this stochastic dynamic behavior.

In this model, CP is predicted to regulate filament growth by controlling the availability of barbed-ends for addition of profilin-actin complexes and the re-growth of recently severed filaments. Loss of CP function should result in an increased number of filaments in cells and an altered behavior of filament ends. To test this hypothesis, we used VAEM imaging to quantify the behavior of single actin filaments in cpb-1 homozygous mutant seedlings expressing the GFP-fABD2 reporter. Dark-grown hypocotyls of cpb-1 are significantly longer than wild-type hypocotyls and their epidermal cells have altered actin organization. Using a newly-developed set of quantitative imaging tools on sets of VAEM snapshots, we found that the actively-growing epidermal cells from cpb-1 have a significantly higher percent occupancy or density of the actin filament array and a corresponding reduction in filament bundling. Time-lapse imaging revealed the bases for these changes in cytoskeletal architecture: single actin filaments in the cpb-1 epidermal cells are significantly altered for several parameters of turnover, especially those that affect the properties of filament ends. Specifically, actin filaments in cpb-1 anneal to each other with 4-fold higher frequency and have significantly longer maximum lengths and lifetimes compared to wild type. Moreover, the number of growing filaments that originate from pre-existing ends is increased in cpb-1, whereas filament growth rates are not altered. To our knowledge, this is the first direct evidence for the regulation of filament barbed-ends by CP in any eukaryotic cell, and provides compelling support for our stochastic dynamics model of turnover. We will confirm the genetic bases for the disruption of actin architecture and single filament dynamics by examining two other cp mutant alleles (cpa-1 and cpb-3) and we will prepare a paper reporting these findings in the near future.

Elucidating the Principles that Control Proton-Coupled Electron Transfer Reactions in the Photosynthetic Protein, Photosystem II

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The solar water-splitting protein complex, photosystem II (PSII), catalyzes one of the most energetically demanding reactions in Nature by using light energy to drive a catalyst capable of oxidizing water. Proton-coupled electron transfer (PCET) reactions, which are exquisitely tuned by smart protein matrix effects, are central to the water-splitting chemistry of PSII. Elucidating the water-splitting chemistry of PSII is of major importance in designing bio-inspired catalytic systems for solar fuels production. Proton motion coupled to electron transfer is the basic mechanism of biological energy conversion. However, the details of PCET processes are not yet understood because of the inability of conventional methods to directly probe PCET processes. A major challenge is to develop methods to directly probe PCET processes to understand the structural requirements for minimizing the energetic penalty for multiple charge transfers. The objective of our research program is 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 propose to determine the factors that control the coupling of proton (PT) and electron transfer (ET) pathways at the Mn_4Ca-oxo, tyrosine and quinone cofactors of PSII by the development of new state-of-the-art multi-dimensional and time-resolved nuclear magnetic resonance (NMR), pulsed electron paramagnetic resonance (EPR) spectroscopy and computational methods. Our research addresses the urgent need for bio-inspired molecular assemblies for new and efficient catalysts for solar fuels production that incorporate the fundamental principles of multi-electron transfer and PCET reactions.

Maximizing Photosystem II Water Oxidizing Efficiency Through the Identification of Optimal Protein Coordination Environments

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The D1 protein of PSII provides most of the ligating amino acid residues for the Mn_4CaO¬5 core of the WOC. Most cyanobacteria have 3-5 copies of the psbA gene coding for at least two isoforms of D1 that are used to adapt to varying environmental conditions, notably light intensity. By expressing natural or unnatural psbA sequences in the model green alga Chalmydomonas reinhardtii, we can compare the efficiency of photosynthetic water oxidation as a function of D1 protein in a single background. This project aims to identify the correlation between D1 sequence and WOC catalytic fitness.

Significant areas of research during our first year of funding (9/1/10 – 8/31/11) include the following:

(a) Eighteen D1 mutants in Chlamydomonas have been constructed by the Mayfield Laboratory (UCSD). These include strains containing heterologous D1 sequences from Arabidopsis thaliana, Thalassiosira pseudonana, and Synechococcus sp. PCC 7942 (both D1.1 “low light” and D1.2 “high light” isoforms), as well as point mutations designed to target specific amino acid differences between varying isoforms.

(b) The Dismukes Laboratory (Rutgers University) is actively analyzing strains constructed by the Mayfield Laboratory (UCSD), as well as previously constructed Synechococcus mutants from the Golden Laboratory (UCSD). Most notably, a distinct phenotypic difference has been identified in Chlamydomonas mutants containing either the “low light” or “high light” D1 isoforms found in cyanobacteria.

We tentatively attribute this difference in water oxidizing efficiency (estimated both through Kok cycle modeling and model-independent Fourier Transform analysis) to secondary charge recombination within PSII, likely involving intrinsic electron donors other that water (including QA-, YD•, cyt b559) that are more active in PSII centers containing the high light D1 isoform.

Structural and Functional Proteomic Analysis of a Developing Energy Transducing Membrane

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While much is known about the light reactions of photosynthesis in purple bacteria and the mechanisms regulating levels of the participating light-harvesting (LH) and reaction center (RC) complexes, comparatively little information is available on how these integral membrane proteins are assembled, how their pattern of localization is established within the cell, or how their apoproteins cooperate with numerous assembly factors in their insertion into the growing intracytoplasmic membrane (ICM). This problem was approached through a detailed structural and functional proteomic analysis of the ICM assembly process in the well-characterized purple bacterium Rhodobacter sphaeroides. Proteomic approaches have focused upon identification of membrane proteins temporally expressed during ICM development and spatially localized in both membrane growth initiation sites and in mature ICM vesicles. Protocols were established for ICM induction under reduced aeration and ICM remodeling in cells adapting to low intensity illumination, which permitted isolation, in sucrose density gradients, of ICM growth initiation sites as an upper pigmented band (UPB) and mature ICM vesicles as the main (chromatophore) band. Non-denaturing clear native polyacrylamide gel electrophoresis (CNE) of these isolated membrane fractions gave rise to pigmented bands containing the peripheral light-harvesting 2 (LH2) antenna and the reaction center (RC)-LH1 core complex, together with a full array of other ICM proteins, which were subjected to proteomic analysis.

Proteomic analysis of the CNE gel bands from chromatophores revealed developmental changes including increasing levels of the LH2 complex as ICM development proceeded, as well as a large array of other associated proteins including high levels of the F1FO– ATP synthase subunits, given the inability to detect this coupling factor, as well as the more abundant cytochrome bc1 complex by atomic force microscopy (AFM). Significant levels of general membrane assembly factors were also encountered, as well as high counts for RSP6124, a hypothetical protein of unknown function, correlated with increasing LH2 levels. RC-LH1-containing CNE gel bands from the UPB were enriched in cytoplasmic membrane (CM) markers, including electron transfer enzymes and transport proteins, as well as general membrane assembly factors relative to equivalent chromatophore bands. This confirms the origin of the UPB from both peripheral respiratory membrane and sites of CM invagination. Significant levels of the preprotein translocases YidC, YajC and SecY, bacterial type 1 signal peptidase and twin arg translocation subunit Tat were found. Such general membrane assembly factors were significantly enriched in the RC-LH1 gel bands from the UPB, confirming the active role of membrane invagination sites in pigment-protein complex assembly.

Functional correlates of these proteomics approaches were provided by near-IR fluorescence induction/relaxation transients arising from the LH-BChl components during low-light adaptation and ICM induction. A linear relation was found between the increasing functional absorption cross-section and the slowing of the RC electron transfer turnover rate, ascribed to the imposition of constraints upon free diffusion of ubiquinone redox species between the RC and cytochrome bc1 complex as the membrane became saturated with new LH2 rings.

In cells undergoing ICM induction in which generation of the electrochemical proton gradient was uncoupled with CCCP, a blockage in the membrane insertion of the LH and RC polypetides was demonstrated. This was reflected in a diminution of the quantum yield of the primary charge separation, a cessation in expansion of the functional absorption cross-section and a >4-fold slowing in the RC electron transfer turnover rate. The ICM insertion of ATP synthase, transhydrogenase and enzymes of photopigment synthesis was also significantly diminished. Importantly, for the UPB fraction, CCCP treatment resulted in accumulation of ~2-fold greater levels of the preprotein translocase SecY, the SecA translocation ATPase, Sec D and SecF insertion components, and chaperonins DnaJ and DnaK, suggesting that these general membrane assembly factors had accumulated in association with nascent LH and RC assembly intermediates. This is attributed to a requirement for an electrochemical proton gradient for the stable insertion of the LH and RC apoproteins into the membrane.

In addition to the spectrally homogeneous bands containing the LH2 and RC-LH1 complexes, CNE also gives rise to two intermediate complexes of intermediate migration, an upper one enriched in LH2 and lower LH1-enriched band, which has facilitated the in vivo assessment of LH2:LH1 associations that may exist in the membrane. For chromatophores from cells adapting to low light intensity, the LH2 CNE gel band was enriched in LH2 polypeptides encoded by the puc1 light-responsive operon, suggesting that these LH2 complexes arise from LH2-only domains formed when LH2-LH1 associations are complete. In contrast, the high levels of LH2 polypeptides encoded by the puc2 operon and the absence of alterations in Puc polypeptide distribution in the upper intermediate LH2-LH1 gel band indicate that it arises from ICM regions laid down early in the ICM remodeling process, in which LH2 is sandwiched between rows of aligned dimeric LH1-RC core complexes.

Analysis of Ethylene-Regulated Growth Networks in Arabidopsis

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The gaseous hormone ethylene plays an integral role in plant growth by regulating the expression of a diverse set of genes. To elucidate how individual hormone signaling pathways are regulated by cis-regulatory circuitries, how these circuitries facilitate cross-communication with other hormone pathways and how they coordinate the establishment of effective defense mechanisms, a comprehensive and genome-wide annotation of functional cis-elements is necessary. Since no genome-wide annotation maps of functional cis-elements exist in Arabidopsis, we aim to generate genome-wide in vitro and in vivo maps of the cis-regulatory landscape. These experiments will uncover how the mutual crosstalk of ET and other signaling is manifested at the level of TF-binding.

To characterize the transcriptional response mediated by ethylene, we used ChIP-Seq and mRNA-Seq to generate genome-wide temporal profiles of transcription factor binding and expression. We found EIN3 (ETHYLENE INSENSITIVE3), a master regulator of the ethylene transcriptional response, targets >1400 genes. Binding by EIN3 increased over time upon ethylene treatment, corresponding with the accumulation of EIN3 protein. A subset (~30%) of EIN3 targets was ethylene-regulated; the majority up-regulated upon ethylene treatment. EIN3 binds three general classes of targets: (1) downstream effectors of the ethylene response; (2) ethylene signaling pathway genes, indicating a major role for feedback regulation of ethylene responses; and (3) key signaling pathway genes involved in other hormone responses (e.g., JA, ABA, auxin). Finally, the role of EIN3 in ethylene-auxin cross-regulation was confirmed when we found EIN3 targeted HOOKLESS1(HLS1) and two of its homologs. HLS1 is a putative N-acetyltransferase regulating the protein levels of AUXIN RESPONSE FACTOR2; a mutant in HLS1 is deficient in establishing the ethylene response apical hook phenotype.

In summary, our temporally-resolved hormone-specific signatures will aid in unraveling the dynamics of TF appearances and disappearances on the network level and on the single gene level, providing a new view into the molecular architecture of plant growth and biomass production.

Signal Transduction Pathways that Regulate CAB Gene Expression

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Chloroplasts of higher plants contain about 3,000 proteins of which more than 95% are encoded by nuclear genes. This necessitates a tight coordination of gene expression that involves two-way signaling between these spatially separated genomes. Thus, while plastid differentiation and development are largely under nuclear control, developmentally arrested or damaged plastids can regulate expression of a subset of nuclear genes via retrograde signaling pathways. In previous DOE-funded studies, we utilized a molecular genetic approach to select for Arabidopsis mutants (gun mutants) in the retrograde signaling pathways. Our data implicate the tetrapyrrole biosynthesis pathway as a source of a retrograde signal, with heme being the most likely signal. We are exploring how heme signals are relayed to the nucleus. In addition, we are continuing genetic and biochemical dissection of the signaling pathway(s) initiated from changes in photosynthetic electron transport redox state in response to excess light. Our screens have already identified seven new genes involved in acclimation to excess light; we will assign these genes to a genetic pathway, and determine the molecular mechanisms by which plants acclimate to excess light. The successful completion of the proposed projects should allow us to begin to engineer these crucial pathways. Since heat, cold, and high light stress share at least some common signaling elements, generation of new genotypes will ultimately influence our abilities to manipulate plant growth and development, and will aid in the understanding of the developmental control of photosynthesis.

Eukaryotic Initiation Factor 3 (EIF3) and 5' mRNA Leader Sequences as Agents of Translational Regulation in Arabidopsis

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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 as follows. (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 to understand 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.

Folding and Function of Proteorhodopsins in Photoenergy Transducing Membranes

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Funding:	$170,000

Proteorhodopsins are a large family of light-driven proton pumps found throughout the world's oceans, fresh water lakes, soil crusts, and most recently on the surfaces of plant leaves. Their measured concentration in the Pacific predicts that proteorhodopsins in ocean surface waters continuously convert solar light energy into transmembrane proton electrochemical potential (protonmotive force) at a rate of ~10^13W, roughly equal to the energy consumption rate of fossil fuels by the human population. Proteorhodopsins consist of a single protein molecule of ~25 kDa that fold into 7 transmembrane a-helices that form a pocket for the chromophore retinal. They have attracted interest because of their simplicity as single-protein solar energy converters, their importance to the energy of the biosphere, and also for their potential as photoenergy-transducing nanomachines for bioengineering applications. This project uses the family of 122 full sequences and >4000 partial sequences of proteorhodopsin variants as target proteins to examine how the primary sequences of a-helical membrane-spanning proteins affect their expression in membranes, their stability in membranes and detergents, their crystallization in cubic lipid phases, and ultimately their structures and function.

Genetic selection schemes with high selective pressure will allow isolation even of rare single or multiple mutations that increase expression of light-driven proton pumping activity by mutant proteorhodopsin variants. Correct folding will be assessed by high-throughput assays measuring the formation of the photochemically reactive retinal-binding pocket. The pocket is comprised of residues from each of the seven helices folded into their native positions to produce characteristic laser flash-induced photochemical reaction cycles and charge displacements amenable to sensitive laser flash kinetic spectroscopy and photoelectrical measurement in vivo, in membranes, in detergent, and in lipid matrices. Rational and random mutagenesis will be applied to increase protein expression, protein stability in detergents, and protein crystallizability, and to determine sequence determinants of these properties. Cubic lipid phase and bicelle crystallization for x-ray structure determination, which we and others have found successful with other microbial rhodopsins, will be applied to 2-3 of the most stable, most highly expressed mutant proteorhodopsins. Added to the existing 7 microbial rhodopsin atomic-resolution structures, this set of structures would be large compared to other membrane protein families and provide a much needed resource to bioinformatics and structural genomics.

The project aims to (1) produce a database providing target selection criteria for expression, stability, and structure determination of other a-helical membrane-spanning proteins and (2) provide a benchmark for structural genomics initiatives; the experimental data set of closely and distantly related rhodopsin structures will be a resource to the bioinformatics community to test and refine homology modeling algorithms for a-helical membrane-spanning proteins. Furthermore, the work will produce high-level expression of stable robust forms of functional proteorhodopsins, a simple and efficient solar energy bioconverter that has great potential for efficient capture and conversion of solar energy in a cost-effective manner. Therefore, this project has potential as fundamental research that will lead to key discoveries and conceptual breakthroughs for solar energy converting materials. The experiments are expected to provide fundamental structural, chemical and biophysical knowledge required to improve natural light-harvesting and energy transformation systems, as well as for the design of biomimetic solar conversion systems.

Biochemical and Molecular Genetic Analysis of the AT-hook Nuclear Localizing (AHL) Gene Family in Arabidopsis

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Funding:	$120,000

The main objectives for our project titled “Biochemical and molecular-genetic analysis of the AT-hook nuclear localizing (AHL) gene family in Arabidopsis” are based on four specific aims:

Aim 1 focuses on testing the hypothesis that the SOB3 interaction network includes AHL family members and possibly other proteins in addition to ESC and HRC. We have made significant progress on this aim, demonstrating that not all AHL family members interact equally. To date our studies have been focusing on BiFC and yeast-two-hybrid (Y2H) analysis. In this final year we will finish those pairwise studies and use pull-down or co-immunoprecipitation (co-IP) assays to confirm these interactions in vitro and in vivo. As a part of this aim, we performed a blind Y2H screen to identify AHL and non-AHL interaction partners. This approach has identified AHL20 and AHL23 as interactors with ESC/AHL27. We have also identified two transcription factors (an AP2-family member and ATAF2), histone H3, histone H4 and a methyl transferase as AHL interactors. AHL interactions with these other DNA-binding or DNA-associating proteins will also be confirmed by BiFC and pull-down/co-IP analysis.

Aim 2 tests the hypothesis that the PPC domain is responsible for protein-protein interactions and the biological functions of AHL family members. We have made significant progress on this aim using Y2H and BiFC analysis. In the final year we will focus our efforts on size exclusion chromatography (SEC) to complement the previous findings that the PPC domain is necessary for AHL-AHL interactions. SEC will also allow us to test the hypothesis that AHL proteins in plants form trimers. In the final year we will also characterize transgenic plants expressing truncated versions of the AHL proteins that include or exclude the PPC domain. Most of these constructs have been transformed into plants and are either at the T1 or T2 stage of analysis.

Aim 3 tests the hypothesis that the AT-hook motif is necessary for SOB3’s interaction with DNA and that the sob3-6 and sob3-5 mutations interfere with this interaction. The primary approach that we proposed, EMSA, requires expressing full-length AHL proteins. In the final year we will focus our efforts on different expression approaches to circumvent the current problem of proteins being sequestered in inclusion bodies. As an alternative approach we are currently developing a targeted yeast-one-hybrid method to test the hypotheses described above. The Neff lab has significant experience with this method for identifying and characterizing proteins that bind DNA.

Aim 4 tests the hypothesis that AHL family members have both shared and unique roles in plant growth and development. As indicated by the reviewers of our proposal, using a loss-of-function (LOF) genetic approach to test this hypothesis is a top priority. In the final year we will focus our efforts on generating higher order LOF combinations with AHLs that are included in the SOB3/ESC co-expression network as well as those that are not. We have already generated and begun characterizing multiple triple-LOF lines and are in the process of generating multiple quadruple-LOF lines. Our preliminary analysis indicates that this will be a productive approach to separate those AHL family members that are involved in seedling development from those that are not.

By the end of this final year of support we anticipate having the data necessary to present our findings in at least one peer-reviewed publication. This final year of support will also allow us to further examine the role of the AHL gene family in energy acquisition, agricultural applications or cellular/plant development. With this information we will decide if this project is more appropriate for DOE or another granting agency.

Disruption of C4 Photosynthesis by Changes in Light Quantity and Quality: Implications for CO_2 Fixation and Photosynthetic Efficiency in C4 Crop and B

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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 1 Undergraduate(s)
Funding:	$170,000

The long-term goal of our research is to determine the mechanisms controlling the metabolic coordination of C4 photosynthesis and the plant's ability to capture, store, and mobilize solar energy. The overall objective of this proposal is to determine the mechanisms controlling C4 photosynthetic efficiency in response to changing light quantity and quality. Fluctuations in light availability are predicted to have a strong impact on C4 photosynthesis, which requires coordination of the C4 and C3 cycle between two cell types. Our central hypothesis is that changes in light quantity and quality will alter the supply of photosynthetic energy (ATP and reductant) to C4 photosynthesis and decrease the energy use efficiency of the CO_2 concentrating mechanism. This hypothesis stems from our preliminary data and previous publications showing that low light decreases the efficiency of C4 photosynthesis, and that the rates of C4 photosynthesis decrease under blue light compared to red and green. The rationale for this research is that it will provide critical information on the efficiency of the CO_2 concentrating mechanism in C4 plants in response to changes in light energy availability, and suggest how C4 photosynthesis may be optimized to obtain the theoretical maximal energy conversion efficiency to help meet our current and future bioenergy requirements.

By combining instrumentation and techniques not currently available elsewhere in the world, outcomes from this novel approach will provide a quantitative measure of the efficiency of C4 photosynthesis under different light environments and determine how changes in the balance of ATP and reductant production dictates the efficiency of C4 photosynthesis. This information will increase the accuracy of mathematical models of C4 photosynthetic response to environmental conditions used in predicting C4 primary productivity and is critical to understanding the potential of C4 plants to help meet our current and future global energy and food requirements.

Enhancement of Photoassimilate Utilization by Manipulation of the Starch Regulatory Enzymes ADPglucose Pyrophosphorylase and Starch Phosphorylase

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Funding:	$170,000

ADPglucose pyrophosphorylase (AGPase) and the plastidial phosphorylase (Pho1) are two regulatory enzymes whose catalytic activity is essential for starch granule synthesis. Conversion of the pre-starch granule to the mature form is dependent on AGPase, which produces ADPglucose, the substrate used 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. Specific questions that remain unanswered are:

- Why is the higher plant AGPase enzyme composed of a pair of large subunits (LSs) and a pair of small subunits (SSs)?
- What are the exact roles of each of these subunit types in enzyme catalysis and allosteric regulation?
- What is the exact contribution of this enzyme in controlling starch metabolism in photosynthetic and sink organs tissues?
- Does starch metabolism influence photosynthetic capacity and, in turn, plant productivity?

Our current efforts on the biochemical properties of this enzyme have demonstrated that the LS and SS possess completely dissimilar catalytic and allosteric regulatory properties with the SS being catalytic and allosteric-defective, and the LS being catalytically-defective and allosteric insensitive. Despite these widely disparate properties, the allosteric regulatory and catalytic properties of the oligomeric enzyme are a product of synergy of LS to SS interactions. In addition to these biochemical studies, physiological studies of this enzyme have been conducted in both photosynthetic and sink organs. We had earlier demonstrated that this AGPase catalyzed reaction is limiting in rice seed starch formation and that carbon flux into rice seed starch can be increased by expression of a cytoplasmic-localized, un-regulated bacterial AGPase. More recent studies have demonstrated that AGPase limits carbon flux into leaf starch and that enhancement of this activity increases the use of leaf starch as a transient sink to accommodate excess photosynthate, a condition which leads to potential photosynthetic feedback and, in turn, suboptimal plant growth.

During the past funding period, this project was extended to starch phosphorylase Pho1 as genetic studies provided direct support for a biosynthetic role for this enzyme during the initial phase of pre-starch formation and its maturation to a starch granule. Although Pho1 catalyzes a reversible reaction enabling it to extend or degrade starch, studies supported by our present DoE grant showed that the kinetic properties of this enzyme strongly favor synthesis. Enzyme activity is inhibited by ADPglucose, suggesting that this catalytic activity is compromised during the maturation phase of starch granule formation, but remains active at the pre-starch granule phase.

In this grant application we propose to continue our comprehensive and integrated research program to study these starch regulatory enzymes. Specifically, we will (1) determine the substrate and effector binding properties of AGPase homotetrameric LS and SS forms and heterotetrameric LS-SS forms; (2) determine the X-ray crystal structures of potato AGPase heterotetramer and rice type L a–glucan phosphorylase Pho1; (3) manipulate carbon flux and increase plant productivity in Poplar (Populus trichocarpa Nisqually-1 by the introduction and expression of up-regulatory AGPases; (4) elucidate the control of Pho1 by post-translational modifications and by interacting proteins and; (5) determine the role of the unique L80 peptide of Pho1 in starch synthesis. Results from these biochemical and physiological studies will increase our fundamental understanding on how these important starch regulatory enzymes operate at the molecular level and in plants, which will aid efforts to increase the utilization of plants as a renewable source of energy.

Controlling Electron Transfer Pathways in Photosynthetic Reaction Centers

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Funding:	$194,000

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.

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+QB- 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 laboratory of Christine Kirmaier and Dewey Holten at WU. The Blankenship lab at WU provides DNA for the generation of the Chloroflexus mutagenesis system.

Mechanism of Solar Energy Storage by Chlorosome Antennas of Green Photosynthetic Bacteria

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Funding:	$201,000

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 both 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 described here 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. It has been studied in great detail using numerous types of structural, spectroscopic and theoretical methods. The FMO protein is probably the most thoroughly studied photosynthetic antenna complex, and was the first chlorophyll-containing protein to have its X-ray structure determined more than 30 years ago. It has continued to be an extremely fruitful system to deepen our understanding even further. We have worked with several other research groups to provide new information about the FMO protein using techniques of ultrafast laser spectroscopy, X-ray crystallography and mass spectrometry. Current research involves the production and detailed analysis of site-directed mutants of the FMO protein. Mutants have been prepared in our group and their characterization is under way.

Novel Factors in the Thylakoid Lumen that Regulate Photoprotection and Repair of the Photosynthetic Apparatus in Cyanobacteria

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Funding:	$180,000

Cyanobacteria are the largest and most diverse group of oxygenic photosynthetic prokaryotes that play major roles in biological carbon sequestration on our planet. They are also the progenitors of chloroplasts in plants and eukaryotic algae. Production of oxygen from water by the Photosystem II (PSII) pigment protein complex in the lumen 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 focus of this proposed project is to determine the mechanisms of newly identified thylakoid lumen localized redox proteins in photoprotection and repair. Hydrogen peroxide (H_2O_2) is a well-known ROS and can damage many important biomolecules such as proteins and lipids. Partial oxidation of water on the donor side of PSII produces H_2O_2, which can result in photoinhibition of the photosynthetic apparatus. We have recently determined that PrxQ-B, a lumen localized peroxiredoxin in the cyanobacterium Synechocystis 6803, is an important determinant in the protection of PSII against photoinhibition. A key hypothesis to be tested is that PrxQ-B is involved in the reduction of H_2O_2 generated by damaged or partially assembled PSII centers. We will also examine the potential role of DsbD-like proteins as transmembrane thiol exchangers that mediate transfer of reductants from the cytoplasmic side of the thylakoid membrane to the lumen, thus providing a redox conduit to proteins such as PrxQ-B.

The specific aims of this proposal are to (1) determine the mechanism for photoprotection of PSII centers by PrxQ-B and (2) define other lumenal factors that are involved in such a protection and repair process. These studies are expected to define a novel pathway in oxygenic photosynthetic organisms to ameliorate the harmful effects of ROS.

Amino Acid-Sensing Ion Channels in Plants

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Funding:	$170,000

Plants possess genes homologous to those encoding glutamate-gated ion channels in the central nervous system of animals. In animals, these membrane proteins form channels that conduct cations including K^+, Na^+, and Ca^{2+} into a cell after the neurotransmitter glutamate binds to them. The molecular-level activities of the plant glutamate receptors (there are 20 GLRs in Arabidopsis) and their roles in plant growth and development are the main subjects of this DOE project. The molecular-level activities are studied with biophysical assays: measurements of membrane potential in plant cells during treatment with amino acids, and voltage-clamp measurements of transmembrane ionic currents in cultured mammalian (HEK) cells expressing Arabidopsis GLR proteins, in some cases with a YC3.6 FRET-based Ca^{2+} sensor protein. A recent key advance is the demonstration that the GLR3.4 channel conducts Ca^{2+} across the plasma membrane after activation by asparagine, glycine, or serine but not other amino acids. The roles in plant growth and development are being investigated by determining where in the plant the GLR proteins are expressed with confocal microscopy, and by studying the root systems of glr knockout mutants. A recent key advance is the finding that GLR3.2 and GLR3.4 are both expressed in the phloem cell of the root. Knockout of either gene causes the primary root to over-produce and misplace lateral root primordia. GLR3.3 is expressed in root cells other than the phloem. Mutation of this GLR gene does not affect production of lateral root primordia. Together, these results indicate that amino-acid sensing by GLR3.2 and GLR3.4 in the root vascular system is coupled by Ca^{2+} signals to the production of new root organs. Research into the physical and genetic interaction between GLR3.2 and

GLR3.4 is underway. This project promises to discover a mechanism by which the carbon:nitrogen balance in the transport system of plants is sensed and influences development.

Molecular Mechanism of Energy Transduction by Plant Membrane Proteins

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Funding:	$130,000

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, including higher plants. The plasma membrane pump, carrier, and channel proteins together convert the chemical energy of ATP into gradients of organic and inorganic solutes. Other plasma membrane proteins, including receptors and protein kinases, help regulate the transporters in a coordinated fashion to respond to environmental changes. Because plants cannot simply move away and escape from harmful environmental conditions, these proteins are part of complex biochemical mechanisms that plants have evolved to minimize the negative impact of nutrient starvation and other environmental stresses. For the past two decades, our laboratory has been developing and implementing genomic and proteomic technologies that allow us to reveal the molecular details of these unique coping mechanisms. Specifically, we have developed and used methods for creating ‘knockout mutations’ in the genes encoding transporters and the proteins that regulate them. We have also developed and used new methods for profiling genetically and environmentally induced changes in the transcriptome, proteome and metabolome.

In this project, the main focus is the plasma membrane proton pump, which is an enzyme that produces the protonmotive force used to drive the transport of all other solutes into and out of plant cells. We are using genomic tools for studying the in-situ role of the plasma membrane proton pump (abbreviated AHA, for Arabidopsis H^+-ATPase). The overall goal of this renewal project is to elucidate the role that protein kinase-mediated phosphorylation and single amino acid point mutations play in regulating plasma membrane proton pump activity in response to various physical and chemical conditions. The AHA gene family contains 11 members expressed during various periods of plant growth. Our most recent focus is on AHA1 and AHA2. These two proteins account for the majority of the ATPase activity in the vegetative plant tissue. For the upcoming grant period, we will be employing a combination of molecular genetic and quantitative phosphoproteomic experiments made uniquely possible by progress in the Sussman laboratory during the previous grant period. We have three specific objectives: (1) in planta gene replacement of AHA1/2 with mutants via complementation of the double AHA1/2 knockout plants, (2) nontargeted mass spectrometric analysis of purified AHA 1/2 and their interacting proteins, and (3) targeted AQUA mass spectrometric assay for measuring AHA1, 2, 3 phosphorylation under many environmental and genetic perturbations.

Carotenoid Function in Natural Photosynthetic Systems

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Funding:	$159,000

The objective of this project is to understand how the functions of carotenoid molecules are tuned in natural photosynthetic systems. Carotenoids are the most widely distributed group of naturally occurring pigments. More than 300 different carotenoids are known in animals, plants, and bacteria. About a dozen carotenoids have been selected in the course of evolution of green plants. They play a number of different roles in photosynthetic systems: as light-harvesting pigments, as photoprotective molecules in triplet energy-transfer processes, as singlet oxygen cavengers, and as components that stabilize pigment-protein structures. In addition, photosystem II (PSII) has been found to utilize beta-carotene as a redox center whereby the carotenoid acts as a “molecular wire” to facilitate long-range electron transfer. If oxidizing equivalents generated by PSII are not transferred rapidly to the oxygen-evolving complex, they can cause oxidative damage. This is a unique problem for PSII among the various types of photosynthetic complexes because only PSII generates an oxidant sufficiently strong to oxidize its own chlorophyll (Chl) and carotenoid (Car) light-harvesting pigments. As a result of this propensity for oxidative damage, PSII is distinct from other photosynthetic complexes in having secondary electron donors involving Car and Chl molecules. Thus, PSII is an ideal system for determining the factors that control carotenoid function in natural photosynthetic systems. Specific goals for this proposal include the following:

(1) Characterize the redox-active Car and Chl molecules that function in the secondary electron-transfer reactions of PSII, and determine the sequence of photooxidation and charge-recombination reactions in the secondary electron-transfer pathways.

(2) Investigate the role of carotenoids in photoprotection in natural photosynthetic systems by comparison of the secondary electron-transfer reactions in plant and cyanobacterial PSII.

(3) Develop methods to deliver non-native carotenoids with varied structural properties to a carotenoid-deficient strain of Synechocystis PCC 6803 for assembly of PSII with non-native carotenoids to enable systematic structure/function studies of carotenoids in PSII.

This project will involve multiple biochemical/biophysical approaches, including optical, EPR, ENDOR and Stark spectroscopy, and computational modeling, together with studies of genetically engineered cyanobacterial PSII, and involves collaborations with Peter Nixon (Imperial College), Steven Boxer (Stanford University), and Doug Bruce/Sergej Vassiliev (Brock University), who will contribute expertise in molecular biology, spectroscopy, and computations, respectively. The principles gleaned from studies of natural photosynthetic systems will, on the one hand, provide insight into the function of carotenoids in natural photosynthetic systems and, on the other hand, will be useful for the design of novel photochemically-driven nanoscale molecular devices that incorporate the light-harvesting, “molecular wire” and photoprotection capacities of carotenoids that have been achieved in natural photosynthetic systems.

DOE National Laboratories

Biomimetic Hybrid Architectures for Solar Chemical Energy Conversion

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Funding: $883,000

This program is targeted at the synthesis of new classes of biomimetic hybrid catalysts for solar fuels applications by combining biological and chemical synthetic approaches. 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.

Controlling Electron Transfer Pathways in Photosynthetic Proteins

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Funding: $106,000

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 ANL team. Note that two technicians, who have received considerable training and professional advancement, are working on this project at ANL; this point is noted here because there is no category for listing such personnel. In addition, these funds supported an undergraduate intern at ANL during the first summer of the project.

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+QB- 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 laboratory of Christine Kirmaier and Dewey Holten at WU. The Blankenship lab at WU provides DNA for the generation of the Chloroflexus mutagenesis system.

Hierarchical Photosynthetic Systems

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$450,000

Subtask 2, “Light-Induced Structural Dynamics in Photosynthetic Model Systems” of the Hierarchical Photosynthetic Systems program focuses on fundamental mechanisms for solar energy conversion by investigating reaction trajectories for a broader range of molecular excited states, charge carriers and reaction matrices for photosynthetic model systems. This subtask focuses on correlating molecular structures at electronic and atomic levels with the reaction kinetics and quantum yields through courses of photochemical reactions. A combined ultrafast optical, EPR, X-ray spectroscopy and diffraction approach is highlighted in this subtask, which will provide four-dimensional detection (x,y,z,t) for direct structural and dynamic resolution of photosynthetic models in disordered media on multiple time and length scales. The knowledge gained on excited state structure-property correlations can be applied to designs of supramolecular systems. Research in this subtask is targeted at (1) the development of a world-leading time-resolved synchrotron X-ray facility in a for solar energy conversion research, (2) investigation of atomic reorganization coupled to excited-state and PET processes in solution, and (3) investigation of atomic reorganization coupled to excited-state and ET processes in structured media.

An integrated, super-resolution characterization of natural photosynthesis. Operating principles, structure, regulation and repair.

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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 propose to follow protein rearrangements in photosynthetic membranes using a range of cutting-edge imaging techniques, which are ideally suited to reveal the complex structural dynamics of the membrane at different levels of spatio-temporal resolution. The imaging approaches will be 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. This understanding will transform our ability to manipulate and engineer the photosynthetic machinery, provide design principles and models for synthetic solar energy conversion systems that are self-regulating and self-repairing, and open a path towards significantly improving global food and energy crops.

Energy Conversion in Photosynthesis - Mechanism of Water Oxidation and Oxygen Evolution

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Funding: $806,000

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 associated 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 X-ray Raman spectroscopy, and FTIR and electrochemistry to provide complementary information. We are also using single-crystals of PS II and inorganic models in our spectroscopic studies. We are using these techniques to elucidate not only the structure of the Mn_4Ca catalytic complex, but also the changes in the structure as it cycles through the intermediate states, leading 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.

Photosynthesis and Photochemistry - Primary Processes in Photosynthesis

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Funding:	$350,000

Photosynthetic light-harvesting systems are regulated, protected against photo-oxidative damage, self-assembled into supercomplexes, and rely on a subtle balance of electronic interactions to produce a highly robust system. In this project, we apply a multidisciplinary approach that combines genetic and biochemical techniques with ultrafast spectroscopy, electronic structure calculation and dynamical modeling to understand the mechanism(s) by which green plants and algae regulate the efficiency of light harvesting in Photosystem II (PSII). As a crucial part of the work, we need to understand the electronic structure of carotenoids and their interactions with chlorophyll (Chl) molecules.

Photosystem II Water-Splitting

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Funding:	$210,000

The primary goal of this research is to understand structural and functional relationships in photosystem II (PSII) with emphasis on energy transfer, primary charge-separation, and water-oxidation processes that in concert generate photosynthetic reductant in the PSII reaction center (RC). This year we developed a simple, colorimetric assay for quantifying functional manganese (Mn/RC) in PSII membrane fragments, which also works with PSII core complexes and thylakoids. This assay is important since it is easy enough to be performed in an undergraduate biology laboratory, does not require expensive equipment (EPR, AA, or ICP spectroscopy), and will allow many more laboratories around the world to do meaningful work on the photosynthetic water-oxidation process. We also developed a procedure to isolate native CP47 complex found in the core antenna of higher plant PSII and showed that the complex has three distinct bands: a lowest-state emission band near 695 nm (labeled F1) originating from the lowest-energy excitonic state A1 of intact complexes (located near 693 nm and characterized by very weak oscillator strength) as well as emission peaks near 690 nm (FT1) and 685 nm (FT2), originating from subpopulations of partially destabilized complexes. We then demonstrated that varying contributions from the F1, FT1, and FT2 emission bands led to different maxima of fluorescence spectra for (partially degraded) CP47 reported in the literature. The above findings provide important constraints and parameters for excitonic calculations, which in turn offer new insight into the excitonic structure and composition of low-energy absorption traps.

Regulation of Hydrogenase Expression

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Funding:	$235,000

The objective of this research project is to develop fundamental understanding of the regulatory mechanisms involved in partitioning of photosynthetic reductants between the hydrogenase pathway and the Calvin cycle. The former is responsible for the production of molecular H_2 during anaerobiosis, and later is involved in CO_2 fixation in the light. In previous funding periods, our analysis of C. reinhardtii mutant libraries for strains having attenuated H_2 production has led to the discovery of the three maturation proteins that are required for the proper assembly of hydrogenases, and to the discovery of the STA7 isoamylase gene, required for transcriptional expression of the hydrogenase genes. Additional library generation and screening continues, under subcontracts to the Colorado School of Mines (CSM) and the Ohio State University (OSU), and has led to the identification of a cystine desulfurase mutant, and a HYDA1 and HYDA2 double mutant, both of which are defective in H_2 production. Our research has also identified a group of Chlamydomonas FixL proteins that are predicted to encode proteins containing sequences with strong amino acid similarity to the rhizobial heme-binding, O_2-sensing PAS domains but that lack obvious signal transmitter domains. Two of these proteins are up-regulated under anaerobiosis, and we have been investigating whether they are involved in hydrogenase gene regulation. Finally, since the precise DNA regulatory elements controlling hydrogenase gene expression are currently unknown, we are conducting analyses of the promoter regions of HYDA1 and HYDA2 genes to gain insight into sequences involved in regulatory signals.

Structural and Integrational Studies of Hydrogenase

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Funding:	$902,000

The overall goal of the project is to advance understanding of hydrogenase structure-function and the parameters that control charge-transfer and catalytic efficiencies in biohybrid, solar H_2-production systems. The knowledge that is gained will support design and development of more efficient solar-to-H_2 conversion by artificial photosynthetic schemes. Model enzymes and systems being investigated under this project include [FeFe]-hydrogenases (H_2ases) that are coupled to photoactive and conducting nanomaterials, and integrated as electrocatalysts in photochemical cells. The main areas of research are (1) theoretical studies of the H_2ase catalytic site, substrate transfer pathways and protein structure; (2) experimental investigations on H_2ase structure-function, and integration with materials; and (3) linking H_2ases, both native and redesigned, with conducting and photoactive nanomaterials, and photobiochemical cells for characterizing the photochemistry and solar-to-H_2 efficiencies of model catalytic hybrids.

Physical Biosciences

Institutions Receiving Grants

Control of Maize Leaf Differentiation and Biomass Accumulation by the SPL Transcription Factor Family

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Funding:	$134,000

Our project seeks to enhance the biofuel properties of crop plants using the Corngrass1 (Cg1) gene and its targets. Dominant maize Cg1 mutants produce increased biomass by continuously initiating extra axillary meristems and leaves. (Whaley and Leech, 1950) In addition, Cg1 biomass possesses increased sugar levels and is more easily digested. 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 trials of our 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. These results point to the potential utility of this approach for domestication of new biofuel crop plants.

We seek to build on these results by (1) controlling the tissue and temporal expression of Cg1 by using different promoters to drive its expression, (2) elucidating the function of the SPL targets of Cg1 by generating gain and loss of function alleles, and (3) isolating 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. The information derived from these studies can be applied to other potential biofuel crop plants that are not as genetically tractable as maize.

Calcium-mediated Regulation of Proton-Coupled Sodium Transport

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Funding:	$155,000

A critical goal for understanding cellular energy transduction is to uncover mechanisms regulating circulation of ions across biological membranes. These ion currents play a major role in energy capture and support a range of physiological processes including the active transport of nutrients, the removal on toxic ions, the regulation of water balance in the plant, and the spatial control of development. Na^+/H^+ exchangers in the vacuolar (NHX protein) and plasma membranes (SALT OVERLY SENSITIVE, SOS1) couple movement of sodium ions into the vacuole or out of the cell using energy stored in the trans-tonoplast and trans-plasma membrane proton gradients. The activity of these secondary active transport proteins is regulated by the CALCINEURIN B-LIKE10 (CBL10) calcium sensor implicating calcium in the regulation of cellular energy transduction. Through characterization of the biochemical and molecular properties of CBL10 as well as its in vivo function, we have made significant progress in understanding how CBL10 couples changes in cellular calcium levels to the regulation of secondary active transport.

Our studies indicate the following:

(1) Post-transcriptional regulation of CBL10 is important for SOS1 activity during seedling growth in salt. CBL10 is alternatively spliced into two transcripts; CBL10 encoding the characterized, full-length protein and CBL10LONGA (CBL10LA) encoding a truncated protein due to a pre-mature termination codon within a retained intron. When seedlings are grown in the absence of salt, both transcripts are detected; however, in response to salt, levels of the CBL10LA transcript are reduced. Our data suggest a model in which the relative abundance of the two transcripts regulates SOS1 activity to maintain cellular sodium ion homeostasis. The presence of CBL10LA in the absence of salt ensures that SOS1 is inactive. Removal of CBL10LA in response to salt results in CBL10 activation of SOS1 to prevent sodium ions from accumulating to toxic levels in the cytosol.

(2) CBL10 also plays a role the regulation of reproductive development. Successful fertilization during flowering requires the coordinated development of stamens and pistils. Stamens must elongate and anthers dehisce to release pollen onto the stigma while the pistil prepares to receive the pollen and promote growth and targeting of the female gametophyte. When the cbl10 mutant is grown in salt, flowers are sterile due to decreased stamen elongation, reduced anther dehiscence, and abnormal pistil development. Our studies indicate that SOS1 is not involved in regulating flower development and that CBL10 functions in different pathways to regulate vegetative and reproductive development during growth in salt.

(3) Two putative CBL10-interacting proteins are required for vegetative growth in high levels of chloride and in maintenance of growth in short-day conditions. An in silico search for Arabidopsis proteins that might interact with CBL10 resulted in the identification of two components of the Mediator complex involved in the regulation of transcription in eukaryotes. While additional studies suggest that interaction with CBL10 in planta is unlikely, we have shown that these proteins are important for plant growth in high levels of chloride and for maintenance of growth in short-day conditions.

Osmoregulation in Methanogens

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Funding:	$130,000

This DOE sponsored 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 structural characterization of the enzymes in di-myo-inositol-1,2-phosphate (DIP) biosynthesis – inositol-1-phosphate synthase, inositol monophosphate:cytidine triphosphate cytidylytransferase, the membrane-localized 3-phospho-DIP synthase, and the inositol monophosphate/fructose bisphosphatase that finally generates DIP – as a step to understanding what regulates DIP accumulation in hyperthermophiles.

(2) Monitor the 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 inositol monophosphatase to look for weak binding sites of known osmolytes (and related solutes that are not thermoprotectants) as a way of exploring apparent specificity in osmolyte thermostabilization of proteins.

The results of this work should highlight how novel solutes are made, what controls them and provide a molecular picture for some osmolyte specificity. It may also be possible to transfer the T. maritima operon for DIP biosynthesis into other organisms to aid in stress tolerance.

Regulation of Cellulose Synthesis

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Funding: $342,000

The main goal of the project is to understand the mechanisms by which cellulose is synthesized. Toward that end we have examined the functional significance of all the phosphorylation sites on two of the proteins (CESA1, CESA3) in the cellulose synthase complex (Chen et al 2010, and un published) and found that some of the modifications differentially alter the rate of polymerization depending on the orientation of the complex on microtubule bundles. In order to understand how phosphorylation of the complex is regulated we have tested a large number of kinases and identified four kinases that phosphorylate one or more sites on the CESA proteins that comprise the cellulose synthase complex (Wallace et al., unpublished). Characterization of the kinases and the factors that regulate their activity is ongoing. We also recently discovered a new protein (CSI1) that colocalizes with cellulose synthase, binds the cellulose synthase complex and mediates alignment of the complex with the microtubule cytoskeleton (Gu et al., 2010). We have also found that the CSI protein binds directly to microtubules and hypothesized that the CSI1 protein is a linker between the cellulose synthase complex and microtubules (Li et al, submitted). Finally, we have characterized all protein-protein interactions between pairs of CESA proteins and also completed promoter swap experiments in which the ability of CESA proteins involved in primary wall synthesis to function in secondary wall synthesis, and vice versa, have been tested (Carroll, submitted). In general, the different types of CESA proteins have limited interchangeability, suggesting significant divergence of the processes.

ROP GTPase Signaling in the Hormonal Regulation of Plant Growth

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Funding: $170,000

Phytohormones play an important role in the regulation of biomass production in plants, but the molecular mechanism by which hormones such as auxin regulates this process is not well understood. Our goal of this project is to understand ROP GTPase signaling pathways that regulate auxin regulation of plant growth. Three specific aims were proposed. In the first aim, we determined which ROPs are functionally redundant with ROP9 in the regulation of auxin-mediated plant growth. Our second aim was to determine which auxin receptors act upstream of ROPs in the auxin regulation of plant growth; our data suggest that both TIR1- and ABP1-based auxin perceptions regulate ROP signaling. Finally, we aimed to determine ROP effector proteins that participate in auxin signaling, and we have demonstrated that a class of plant-specific ROP effector proteins termed RICs are involved in ROP-based auxin signaling. Our studies have generated new insights into the molecular mechanisms underlying auxin regulation of plant growth.

Trafficking to the Protein Storage Vacuoles in Plants

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Funding: $180,000

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 fit 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.

Molecular and Genetic Basis of Sodium/Potassium Transport and Distribution in Plants

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Funding: $178,000

Salinization of soils is increasingly detrimental to renewable bioenergy production, photosynthesis and metabolism, and limits available land for plant biomass growth. Most plants are sensitive to high concentrations of sodium (Na^+). Sodium concentrations in diverse cellular compartments and plant tissues are regulated by the activity of Na^+-transporting membrane proteins. Potassium (K^+) is crucial for growth and development and competes with Na^+. Identification and characterization of the molecular and biophysical mechanisms mediating Na^+ and K^+ transport throughout plant tissues and cell organelles is pivotal to understanding plant growth and can allow engineering of salt tolerant plants. The long-term goal in this research field is to understand the roles of individual Na^+ and K^+ permeable transporter types and individual genes in mediating salt tolerance. In the present proposal the molecular and biophysical functions of HKT-type transporters will be characterized, with a particular focus on the single Arabidopsis gene AtHKT1;1 and rice OsHKT genes. We have reported a recently recognized function of the Arabidopsis Na^+ transporter, AtHKT1;1. ICP, immuno-localization and other analyses suggest a model in which AtHKT1 functions in removing sodium from the xylem sap of Arabidopsis plants during salinity stress. This in turn, results in protection of plant leaves from Na^+-induced chlorosis, where Na^+ causes major damage by inhibiting photosynthetic and metabolic processes.

Grasses are considered as prime candidates for renewable biomass production, and rice provides a well-developed genomic/genetic grass model system. Recent research in rice and wheat indicate that major salt tolerance QTL may be encoded by orthologs of AtHKT1;1 with analogous functions in removing Na^+ from the xylem. We have recently identified a first mutation in a Na^+ transporter gene, oshkt2;1 in rice, that greatly diminishes $^{22}Na^+$ influx into plant roots. K^+ starvation-induced OsHKT2;1-dependent Na^+ influx into rice roots is rapidly down-regulated by salinity stress. We will characterize both AtHKT1;1 and OsHKT2;1 functions. Interestingly, a second "class-2" family of HKT proteins that shows increased relative K^+ permeability in heterologous systems has thus far only been identified in grasses. Rice is a genetically and genomically tractable system in which both classes of HKT transporters can be characterized in the same plant. We will use homozygous gene disruption double mutant alleles in the only class-2 Nipponbare rice members, that show a unique "4 glycine" pattern in their cation selectivity filter domains, OsHKT2;3 and OsHKT2;4 and will further analyze OsHKT2;1. This will allow direct investigation of predicted K^+ transporting class-2 HKT transporters. To advance the understanding of mechanisms mediating HKT-dependent salt tolerance and investigate emerging hypotheses we propose to (1) characterize the biophysical transport functions of AtHKT1;1 directly in native xylem parenchyma cells; (2) isolate mutants and characterize physiological transport and salinity tolerance functions in rice of the class-1 OsHKT1;4 and the above class-2 HKT transporters; and (3) initiate research into the functions of OsHKT2;1 and protein regulators/interactors in regulating Na^+ influx into roots.

Salt stress is an increasingly damaging problem for renewable energy and plant biomass production. Results from these studies may contribute to the future development of strategies for engineering improved Na^+/K^+ distribution and reduced sodium damage of photosynthetic tissues for improved growth and light energy conversion by plants.

Proteomic Study of Brassinosteroid Responses in Arabidopsis

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The long-term goal of this project is to understand the molecular and biochemical mechanisms through which BR and light signals regulate gene expression and plant growth and development. 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 light or BR signals; and then study the functions of the identified proteins and mechanisms using combinations of molecular, genetic and biochemical approaches. The specific goals of this proposal include (1) illustrating the functions of a BR-regulated nuclear protein with both DNA-binding and RNA-binding domains that regulates the transition from vegetative to reproductive development and (2) identify additional BR regulated nuclear proteins using improved protocols that yield highly purified nuclei and nuclear subfractions from specific cell types. During FY2011, we have established the nuclei purification method for quantitative analysis of nuclear proteome. We have further characterized the NBR1 gene. More specifically, we have obtained a strong allele of knockout mutant and observed much stronger late-flowering phenotype, confirming NBR1's role on BR regulation of flowering independent of cell elongation. We have purified NBR1 and analyzing is modification and associated proteins using mass spectrometry; we found proteins known to regulate flowering in NBR1 complex and three phosphorylation sites in NBR1. We are characterizing the interacting proteins and functions of the phosphorylation sites. Our results provide strong evidence for an independent branch of BR signaling pathway for regulation of the transition from vegetative to reproductive growth. This provides important information and tools for genetic engineering of the BR pathway for high-yielding plants.

Regulation of Xyloglucan Galactosylation in Arabidopsis

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The cell walls of land plants are composed of several polysaccharides that can broadly be classified as cellulose, hemicelluloses and pectins. Because these polymers account for most of the photosynthetically fixed biomass in plants, they are an attractive source of renewable energy mainly in the form of liquid fuels that can be obtained by microbial fermentation of the constituent sugar moieties. To make the best possible use of this natural resource, it is important to understand the genetic and biochemical processes that lead to the conversion of primary photosynthate to activated monosaccharides via nucleotide sugar interconversion pathways, and their subsequent use by glycosyltransferases to assemble the highly complex polymers.

To achieve this goal, we have been using the hemicellulose xyloglucan as a model system to obtain an integrated view on how plants channel carbon into activated monosaccharides, and subsequently into cell wall polysaccharides. It is well established that the xyloglucan backbone is decorated by galactose moieties at two specific positions but the extent of this modification is highly variable. This raises the question whether the degree of xyloglucan galactosylation is a function of precursor availability, glycosyltransferase activity or both. As part of our DOE-funded project we were recently able to establish that a member of glycosyltransferase family 47 in Arabidopsis (tentatively designated MUR12) acts as a bona fide xyloglucan galactosyltransferase with a different attachment site specificity than the previously characterized MUR3 protein. To determine whether the abundance of either of these enzymes is rate-limiting for xyloglucan galactosylation, we overexpressed the wild-type versions of these genes in Arabidopsis, and found that some of the transgenic plants showed an increased level of galactose attachment at the expected positions. To address the issue whether availability of the donor substrate UDP-galactose is a limiting factor, we overexpressed fluorescent-protein-tagged versions of isoform 2 of UDP-glucose 4-epimerase in the cytosol and as a fusion with a signal-anchor sequence to achieve targeting to the Golgi. Recent results from carbohydrate composition analysis indicate that some of the transgenic plants contain elevated levels of galactose in their cell wall material. This suggests that both precursor availability and glycosyltransferase activity influence the degree of xyloglucan galactosylation. We are now in the process of generating transgenic plants that overexpress both galactosyltransferases and the UGE2 gene simultaneously. Since there is evidence that the wild-type version of the MUR12 gene is not optimal for protein expression in plants, we plan to determine whether a synthetic version of this gene will be more effective in increasing the degree of galactose attachment to the xyloglucan backbone.

From the Soil to the Seed: Metal Transport in Arabidopsis

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Funding:	$160,000

OVERALL RESEARCH GOALS

Deficiencies of micronutrients such as Fe and Zn commonly limit plant growth and crop yields. The long-term goals of our program are 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. With an increased emphasis on growing plants for biofuel production, 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 a Fe 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.

SIGNIFICANT ACHIEVEMENTS

We are continuing to examine metal distribution using XRF in seeds and leaves from a variety of metal transporter mutants. We have been awarded beam time at three different DOE-supported facilities: the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, the Advanced Photon Source (APS) at Argonne National Laboratory, and the Stanford Sychrotron Radiation Lightsource (SSRL). We have recently added a Vortex® Silicon Drift Detector to NSLS beamline X26A that has greatly enhanced our imaging capability and shortened our capture time. This detector is a single element X-ray detector produced from high purity silicon using state-of- the-art CMOS production technology. It features excellent energy resolution (<136 eV FWHM at Mn Ka is typical) and a high count rate capability (input rate >1 Mcps) that are particularly well suited for our applications. At a very short peaking time of 0.25 µs, an output count rate of 600 kcps is achieved. A unique feature of these detectors is their ability to process high count rates with virtually zero loss in energy resolution and no peak shift with count rate. We have used the system to enhance detection of low energy X-ray emissions such as those from Ca Ka, K Ka and S Ka. Enhanced detection of these elements by fluorescence microtomography is crucial for our studies on the elemental composition of plants, but is not possible using existing detectors at the beamline due to self-absorption effects. Installation has not only eliminated self-absorption, but has also allowed the switch to fly-scanning, making scan times appreciably shorter; tomographic sections of Arabidopsis seed now take less than 2 hours to complete (see Punshon et al., 2011 Plant Physiol. doi:10.1104/pp.111.184812), in comparison with approximately 7-10 hours for a high resolution image (see Kim et al., 2006 Science 314:1295). Fly-scanning allows for greater replication, greater accessibility to three dimensional imaging, high-throughput analysis and analysis of fresh, hydrated tissue such as stems, leaves and roots. This past December, we began imaging seed within the developing siliques, at SSRL. We are very excited about these images as we can see Zn accumulating in the vasculature of the silique before it is loaded into the seed.

We have just finished characterizing an Arabidopsis line that overexpresses the vacuolar transporter VIT1 and have compared its iron responsiveness to wild type and as well as to a vit1 loss of function line. Ectopic expression of VIT1 leads to increased iron accumulation in leaves. This increase is accompanied by increased ferric iron chelate activity and increased levels of IRT1 protein, the high affinity iron uptake components in Arabidopsis roots. The loss of VIT1 attenuates the induction of IRT1 protein, resulting in delayed responses to high metal treatment. 35S-VIT1 plants deposit less iron in seeds and display altered iron distribution in the embryo. Not surprisingly, 35S-VIT1 seedlings grow less well than wild type on iron limiting soil. Our results suggests that VIT1, by moderating vacuolar iron content, plays a pivotal role in cellular iron homeostasis and the regulation of iron uptake. We are also characterizing loss of function and over expression lines for the two VIT orthologs in rice. This work is progressing slowly as our collaborator in Korea, Dr. An, recently moved to a new institution.

We were fortunate to receive supplemental funding for this grant in order to acquire a CIRAS-2 Portable Photosynthesis System with FMS-2 Chlorophyll Fluorescence Monitor. This purchase brought a much-needed capability for the measurement of photosynthesis to two BES-funded projects, mine and that of my colleague Eric Schaller. As part of our studies to further characterize Fe and Mn transporters, we need to be able to monitor whether photosynthesis is compromised in loss of function or over-expression lines. Up until now, we have relied on collaborators to carry out measurements of photosynthetic function for us. We will be carrying out these measurements over the next few months.

Fundamental Aspects of Cellulose Utilization

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Funding:	$170,000

BACKGROUND & FUNDING STATUS

Grant Number DE-FG02-02ER15350 was originally awarded for a project with P.I. Lee Lynd (Dartmouth) and co-P.I.s Paul Weimer (University of Wisconsin), and Herb Strobel (University of Kentucky). The duration of the original grant was September 1, 2002 to August 31, 2004 with continued funding awarded in September of 2004 through 2/28/2007. In 2007, a grant was awarded to continue work in the Lynd lab with Lee Lynd as the P.I. entitled “Fundamental aspects of microbial cellulose utilization.” This third grant was for $465K for a 2.5 year period from March 1, 2007 through November 30, 2009 and was extended to April 30, 2011 at no additional cost to DOE.

PROGRESS REPORT

Work was undertaken with the overall objective of advancing fundamental understanding of cellulose utilization by Clostridium thermocellum. The most recent award was made in support of two tasks: (1) the testing of the substrate capture hypothesis in C. thermocellum and (2) the investigation of microbial cellulose hydrolysis based on gene knockout.

Work on both of these proved challenging, and progress was initially slow although very substantial progress was eventually made. Progress on advances and application of genetic tools for C.

thermocellum was reported in the last reporting period. Since that time, significant progress has been made at testing the substrate capture hypothesis through the use of a low carbon media developed in our lab and flowcells developed in collaboration with Ryerson University. We decided to approach this by performing a carbon balance on the supernantant of the flowcell effluent under conditions where there where minimal cells in the effluent and thus minimal opportunity for effluent cells to capture any released hydrolysis products. Under these conditions, we found that 60% of the carbon in the effluent supernatant was in the form of fermentation products (acetate, ethanol, formate, and lactate) and 3% was in the form of potential hydrolysis products (cellobiose as glucose was not detected). While we are looking for ways to quantify carbon remaining due to the media (mostly in the form of cysteine), we calculate that 37% of the effluent carbon is due to media carbon. Since the media has a short residence time (<30 min) within the flowcell, we feel that this is a reasonable assumption; however, before publishing, we plan to further verify this assumption.

Post-Transcriptional Regulation of Ethylene Perception and Signaling in Arabidopsis

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The simple gas ethylene functions as an endogenous regulator of plant growth and development, including such energy-related aspects as bio-mass, cell wall composition, and photosynthetic capacity. 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, with our data indicating that the level of CTR1 is dynamically regulated due to ethylene-induced changes in receptor levels. Low levels of ethylene result in an increase in levels of the receptors and the physically associated CTR1, while higher levels of ethylene result in turnover of the receptors and a concomitant decrease in levels of CTR1. 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, these data suggest that the tremendous range of ethylene receptor signaling capacity is achieved in part by incorporating a variety of regulatory mechanisms.

Engineering Functional Scaffolds by Supramolecular Self-Assembly

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Funding:	$180,000

The design of synthetic nanomaterials continues to benefit from structural investigations of the biological supramolecular machinery that performs the chemical, electrical, and mechanical functions associated with cellular metabolism, communication, energy capture and utilization, and differentiation. The self-assembly of these complex supramolecular machines (e.g., the ribosome, microtubules, translational complexes, etc.) arises from organized association of multiple sub-units via structurally modulated non-covalent interactions that are programmed into the primary biopolymer sequence. As a consequence of the near-absolute control of macromolecular architecture seen in polypeptide and polynucleotide assemblies, learning these rules of assembly could provided structural guidelines for the design and construction of new, well-defined supramolecular assemblies with desired functions.

DOE funding has allowed us to make great progress in developing methods for characterizing self-assembled 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. Examples of the success are seen in the many precisely defined assemblies with functions that range from light harvesting antenna to peptide bilayer membranes to simple catalysts. The development of these functional assemblies however has revealed some remarkable properties that we now argue may be accessed for the creation of new self-organizing materials. More than static structures, or even smart materials that are responsive to a changing physical environment, self-organizing materials have the potential to profit or learn from their environment. Certainly the synthetic genomes that have recently been functionally transplanted into cells can adapt and change, evolve in response to pressure, and thereby learn from their experiences, and hence must be considered materials or networks with intelligence. Intelligent behavior may not be restricted to complex genomes, but a general property of a molecular network, even an inherent property of matter. Therefore, we now propose that it is possible to lay the foundations for the discovery of intelligent materials in a synthetic network.

We assert that the next challenge in bio-inspired material design is “intelligent materials.” Accordingly, we will propose strategies that couple specific reactions into chemical and thermodynamic networks, exploiting the many structural polymorphs accessible to peptide assemblies, to create the diverse foundations that may be essential for the emergence of self-organizing behavior. Our long-term goal will be to expand greatly the supramolecular assembly toolbox by creating synthetic intelligent materials that provide a foundation for a synthetic biology based on new functional materials.

Ubiquitin-Like Proteins in Protein Conjugation and Sulfur Transfer in Archaea

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Archaea are the least characterized among the three domains of life, yet represent a group of microorganisms with tremendous potential toward furthering DOE missions to understand global nutrient cycles, discover new pathways of carbon sequestration and foster a bio-based economy. Archaea contribute to a large fraction of Earth's biomass and have central roles in global inorganic and organic cycles including nitrogen fixation, anaerobic oxidation of methane, methanogenesis and novel pathways of CO_2 fixation. Furthermore, unlike many bacteria, archaea are 'Generally Recognized as Safe' (GRAS) and commonly encode enzymes that can withstand harsh conditions such as boiling water, high concentrations of solvent and extremes of pH. Thus, archaea and their enzymes are ideal platforms for petroleum-independent biocatalytic applications and sustainable chemical processes. Archaea also provide new insight into the breadth of metabolic and enzymatic potential present on this planet with as much as 50% of their genes encoding novel proteins with no obvious counterparts in bacteria or eukaryotes.

The long-term goal of our research program is to elucidate global mechanisms of post-translational regulation in archaea. Investigating these types of systems is not only important in furthering our knowledge of how the three domains of life are related in cellular function, but is also important in advancing our ability to modify pathways for biotechnology applications in extremophilic microbes and facilitate further transition to a biobased economy. Understanding how to engineer tight control of post-translational mechanisms will enable the design of metabolic pathways and enzymes that undergo predictable (and even transient) alterations in activity, covalent protein structure, multisubunit complex formation, protein stability and/or cellular location. Cultivating a deeper knowledge of post-translational control mechanisms will also allow new biotechnology applications to be developed that benefit from the timed synthesis of bioproducts which may be otherwise detrimental to cell function.

Through our work with DOE, we have investigated the role of proteasomes (energy-dependent proteases) in archaea and recently discovered a new type of post-translational control mechanism (termed sampylation) that appears to be biologically linked to proteasomes. In sampylation, small archaeal ubiquitin-like modifier proteins (termed SAMPs) are covalently attached through isopeptide bonds to protein targets by a process that has deep evolutionary roots with the ubiquitin-proteasome system of eukaryotes. The ubiquitin-proteasome system of eukaryotes is a central node for controlling cell division, DNA repair, inflammation, formation of protein aggregates and other important processes. Based on studies performed by our lab group, archaeal homologs of the eukaryotic ubiquitin-activating enzyme E1 and deubiquitylating enzymes of the JAMM/MPN+ superfamily appear to mediate sampylation and desampylation. Interestingly, components of the archaeal sampylation system also appear to be required for the production of sulfur-containing biomolecules such as 2-thiolated tRNA and the pyranopterin-based molybdenum cofactor (MoCo). Thus, our current working model is that ubiquitin- and E1-type proteins are at the crossroads of mediating protein conjugation and sulfur incorporation in archaea.

Center for Plant and Microbial Complex Carbohydrates

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Funding:	$791,000

The Complex Carbohydrate Research Center (CCRC) of the University of Georgia is a national resource for the study of complex carbohydrates. The DOE Center enables the CCRC to provide service and training to academic, government, and industrial researchers who study the complex carbohydrates of plants and microbes by providing support of experts who operate, maintain, and assist in interpreting the data obtained from a variety of scientific instrumentation. The expanding need for expertise in studies of the structure/function of complex carbohydrates is rapidly growing as the importance of carbohydrate research in areas such as biomedical glycobiology, vaccine development, and biomass conversion to biofuels is being recognized.

The DOE Center enables several types of service to be offered to researchers. Scientists who request analytical service(s) receive a written report containing a description of (1) the analytical procedures used, (2) publishable quality results (data) of the analyses of their samples, and (3) an authoritative interpretation of the results. CCRC personnel also provide collaborative service by becoming involved in "in depth" scientific research projects with individuals from other laboratories. Over the past four years, the CCRC has provided analytical service or collaborative service to 350 scientists. CCRC personnel consult with external scientists via e-mail and telephone, helping the scientists address specific analytical problems or interpretation of data. The CCRC’s web site (www.ccrc.uga.edu) provides freely accessible, Internet-searchable databases assisting in aspects of carbohydrate science, a scheduler for shared use of instrumentation, and descriptions of the CCRC's various research projects. The CCRC also provides researchers with often hard to obtain chemical and biological samples.

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, 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.

Fundamental Studies of Recombinant Hydrogenases

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Funding:	$230,000

The proposed research addresses the issues of understanding the assembly and organization of hydrogenase enzymes, of reducing them in size and complexity, of determining structure/function relationships, including energy conservation via charge separation across membranes, and in screening for novel hydrogen gas catalysts. A key overall goal of the proposed research is to define and characterize minimal hydrogenases that are produced in high yields and are oxygen-resistant. Remarkably, in spite of decades of research carried out on hydrogenases, it is not possible to readily manipulate or design the enzyme using molecular biology approaches since a recombinant form produced in a suitable host is not available. Such resources are essential if we are to understand what constitutes a “minimal” hydrogenase and design such catalysts with certain properties, such as resistance to oxygen, extreme stability and specificity for a given electron donor. The model system for our studies is Pyrococcus furiosus, a hyperthermophile that grows optimally at 100°C, which contains three different nickel-iron [NiFe-] containing hydrogenases. Hydrogenases I and II are cytoplasmic while the other, MBH, is an integral membrane protein that functions to both evolve hydrogen gas and pump protons. Two dramatic breakthroughs have been made in the past funding period with P. furiosus soluble hydrogenase I (SHI): (1) we have produced an active recombinant form of SHI in E. coli by the co-expression of 16 genes using anaerobically-induced promoters, and (2) we have genetically-engineereding P. furiosus to overexpress SHI by an order of magnitude compared to the wild type strain. We now have two robust model systems involving heterologous (in E. coli) and homologous (in P. furiosus) expression to engineer different forms of SHI and already have success by reducing the enzyme from a heterotetramer to an active heterodimeric form.

Hypothermophilic Multiprotein Complexes and Pathways for Energy Conservation and Catalysis

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Funding:	$170,000

We are investigating the 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 to be studied in the proposed research have the remarkable property of being synthesized (self-assembling) at temperatures near 100°C in a so-called hyperthermophilic microorganism. Moreover, the novel 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. This is particularly relevant to the DOE mission since a fundamental problem in all photosynthetic reaction systems is the conversion of low potential reductant to a useable form of energy such as an ion motive force. The model system is Pyrococcus furiosus (Pf), which grows optimally at 100°C. Pf obtains carbon and energy for growth by fermenting carbohydrates and producing hydrogen 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 highly homologous membrane complex which we term MBX. MBX is proposed to oxidize ferredoxin, reduce S° and conserve energy by an as yet unknown mechanism. Pf also uses S° reduction for the biosynthesis of iron-sulfur clusters by a novel protein termed sulfur-induced protein A (SipA, 19 kDa). This is purified from Pf as a complex approaching 100 MDa in size that contains approximately 5,000 SipA monomers and 45,000 [4Fe-4S] clusters.

The specific aims of the proposed research are to (1) characterize the novel energy-conserving complex MBH, (2) characterize the novel energy-conserving complex MBX, (3) characterize the iron-sulfur cluster megacomplex SipA, (4) determine the sites of S° reduction and its role in iron-sulfur cluster biosynthesis, and (5) structurally characterize native SHI and minimal forms of SHI and MBH. We will take advantage of the recent development of a genetic system in Pf. 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) and biological syntheses (SipA) 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 small-angle x-ray scattering (SAXS), sulfur and metal x-ray absorption spectroscopy, cryo-electron microscopy, and membrane and soluble protein x-ray crystallography of the various energy-transducing systems under study.

Secondary Wall Formation in Fiber Cells

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Funding:	$181,000

The goal of this DOE-funded project is to study functional roles of glycosyltransferases in xylan biosynthesis during secondary wall formation. Secondary walls are the major constituent of tracheary elements and fibers in wood, which is the most abundant biomass produced by plants. Understanding how secondary walls are produced would not only contribute to our knowledge of basic plant biology but also have economic and environmental implications because wood is one of the most environmentally cost-effective and renewable sources of bioenergy and widely used for lumber and pulping. We proposed to carry out the functional characterization of glycosyltransferases (GTs) involved in the biosynthesis of xylan, the second most abundant polysaccharide in wood.

Xylan is considered to be one of the factors contributing to wood biomass recalcitrance for biofuel production. To better utilize wood as biofuel feedstock, it is crucial to functionally characterize all of the genes involved in xylan biosynthesis during wood formation. We have discovered that GT43 members in both Arabidopsis and poplar are involved in xylan biosynthesis and that they form two functionally non-redundant groups essential for the normal elongation of xylan backbone. Further biochemical studies have revealed that GT43 glycosyltransferases from both Arabidopsis and poplar possess xylosyltransferase activity when expressed in tobacco BY2 cells, indicating that they are the long-sought xylan synthase. This is an important advance in our understanding of the biochemical mechanism underlying xylan biosynthesis because none of glycosyltransferase genes have so far been proven enzymatically to be involved in xylan biosynthesis. We have also found that three Arabidopsis glycosyltransferases belonging to family GT8 are glucuronyltransferases involved in the addition of glucuronic acid side chains onto the xylan backbone. We performed comprehensive genetic and functional studies of four Arabidopsis REDUCED WALL ACETYLATION (RWA) genes and demonstrated their involvement in the acetylation of xylan during secondary wall biosynthesis.

Our successful assays of GT43 and GT8 glycosyltransferase activities have opened a new avenue to biochemically characterize other glycosyltransferases involved in xylan biosynthesis. We expect that our work will lead to a better understanding of the biosynthesis of xylan, one of the major wood components and provide tools for custom-designing wood components tailored for biofuel production.

Structural Studies of Complex Carbohydrates of Plant Cell Walls

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Funding: $410,000

Much of the solar energy captured by land plants is converted into the polysaccharides (cellulose, hemicellulose, and pectin) that are the predominant components of the cell wall. These walls, which account for the bulk of plant biomass, have numerous roles in the growth and development of plants. Moreover, these walls have a major impact on human life as they are a renewable source of biomass, a source of diverse commercially useful polymers, a major component of wood, and a source of nutrition for humans and livestock. Thus, understanding the molecular mechanisms that lead to wall assembly and how cell walls and their component polysaccharides contribute to plant growth and development is essential to improve and extend the productivity and value of plant materials. Our studies use the development and application of advanced analytical and immunological techniques to study specific changes in the structures and interactions of the hemicellulosic and pectic polysaccharides that occur during differentiation and in response to genetic modification and chemical treatments that affect wall biosynthesis. These techniques make it possible to accurately characterize minute amounts of cell wall polysaccharides, so that subtle changes in structure that occur in individual cell types can be identified and correlated to the physiological or developmental state of the plant. Successful implementation of this research will reveal fundamental relationships between polysaccharide structure, cell wall architecture, and cell wall function.

Understanding the Mechanism by Which Non-Catalytic Carbohydrate Binding Modules Contribute to Plant Cell Wall Degradation

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Plant cell walls are the most abundant source of organic carbon on the planet. This photosynthetically fixed carbon is recycled by microbial enzymes, a process that is critical to the maintenance of terrestrial and marine life itself. Microbial enzymes that deconstruct plant cell walls are of industrial significance particularly in the production of second generation lignocellulosic-based biofuels and in the bioprocessing sector, where the synthesis of high-value chemicals from renewable sources, such as plant biomass, is of particular importance. Plant cell walls, however are recalcitrant to biological depolymerization as the extensive interactions between polysaccharides restrict access to the battery of microbial enzymes that break down these composite structures. Microbial plant cell wall hydrolases contain catalytic modules that are appended by flexible linker sequences to non-catalytic carbohydrate binding modules (CBMs). In vitro studies have shown that, by binding to polysaccharides, CBMs reduce the “accessibility problem” by bringing the appended catalytic modules into tight association with their target substrate and thereby enhance catalytic efficiency. The nature of the substrates used in these experiments, however, limits their utility as models for the microbial-mediated degradative process in vivo. Recent studies have shown that CBMs that are structurally distinct, but exhibit the same specificities against purified ligands, display differences in their recognition of plant cell walls, which likely reflects the interaction of the target polysaccharides with other components of the cell wall. In view of the complex targeting role CBMs play in vivo, the functional importance of these modules in degrading intact plant cell walls is currently unclear. While it is apparent that these modules will increase catalysis by enhancing enzyme substrate contact, they may also play a role in assembling glycoside hydrolases and/or esterases that display complementary activities into juxtaposition in the cell wall, thereby potentiating the synergistic interactions between these biocatalysts. It is also unclear whether the precise biochemical properties of the catalytic modules of these enzymes are tailored to the specificity of the appended CBMs. This proposal will address the various issues discussed above, concerning the functional significance of CBMs in the depolymerization of the plant cell wall in vivo. The project will test the following hypotheses:

(1) The biological rationale for the diversity of bacterial CBMs found in nature is to maximize the range of plant cell walls that can be degraded by the cognate enzymes.

(2) The essential synergy between glycoside hydrolases that display complementary activities is promoted by CBMs through the targeting of these biocatalysts to the same region of the plant cell wall.

(3) Specific CBMs, which target the ends of polysaccharide chains, direct glycoside hydrolases to regions of cell walls that are particularly susceptible to enzyme attack.

(4) The catalytic module linked to a specific CBM has evolved biochemical properties that are complementary to the targeting function of the appended CBM.

The methods deployed to address these objectives will involve the production of specific enzyme-CBM combinations using recombinant technology. The capacity of these proteins to deconstruct plant cell walls will be assessed using cell imaging methodology, such as fluorescence microscopy where the disappearance of polysaccharides will be quantified using specific labeled cell wall probes.

BENEFITS AND OUTCOME

This project seeks to provide fundamental information on the contribution of CBMs to the enzymic deconstruction of the plant cell wall into its component sugars. By addressing this critical biological question, the research will underpin environmentally significant industrial processes, such as the exploitation of ligno-cellulosic biomass in the production of second generation biofuels and in the production of high value chemicals from a renewable resource.

Genetic Analysis of Hydrogenotrophic Methanogenesis in Methanosarcina Species

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The long-term goal of the proposed research is to expand our knowledge regarding energy-conservation during methanogenesis in Methanosarcina species. A central aspect of this study entails examination of the genotypic and phenotypic differences between Methanosarcina barkeri, an organism that grows well on H_2/CO_2, and Methanosarcina acetivorans, a closely related organism that is incapable of growth on H_2/CO_2. Our recent data show that hydrogen is a central intermediate in methanogenesis from all known substrates in M. barkeri, whereas M. acetivorans has evolved to specifically exclude hydrogen as an intermediate. The differences in hydrogen metabolism lie at the center of the energy-conserving electron transport chains of the two organisms. By examining the molecular, genetic, biochemical and physiological traits that underpin these differences we expect to deepen our overall understanding of methanogenesis, hydrogen production/consumption and energy conservation during anaerobic metabolism; all of which are central themes in the DOE Energy Biosciences research program. Three specific issues regarding the mechanisms of energy conservation in Methanosarcina are addressed in the proposed experiments. First, we will characterize the molecular mechanism of energy conservation via hydrogen-cycling in M. barkeri. Second, we will characterize the hydrogen-independent, energy-conserving electron transport chain in M. barkeri. Third, we will characterize the hydrogen-independent, energy-conserving electron transport chain in M. acetivorans. The proposed experiments will utilize recently developed methods for genetic analysis of Methanosarcina; however, physiological, biochemical and molecular approaches will complement the genetic approach. This strategy is expected to generate data that are both novel and complementary to the results of preceding studies.

Mechanistic Studies of Catalysis in Quinone Electron Transfer Using High-Resolution EPR

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Funding: $200,000

Genomic analysis suggests that approximately one third of all proteins have metallic cofactors or other paramagnetic centers suitable for investigation by EPR. About one third of all proteins are membrane proteins, many of which use effectors acting from the lipid phase. The membrane bound electron transfer proteins contribute a large fraction of the substantial overlap between these two classes. The electron flux through all major electron transfer pathways, - photosynthetic and respiratory chains, for example, - is carried by quinones that functionally link the complexes of respiratory or photosynthetic enzymes embedded in the membrane. The interfaces through which these redox reactions are catalyzed, the quinone processing sites, have properties that are determined by the protein, and differ so as to fit each site to its particular physiological role. Interactions between protein and occupant change the affinities of the site for quinone, semiquinone (SQ) and dihydroquinol forms, orient the occupant for effective electron transfer, and determine pathways by which protons enter or exit. The choreography of catalysis is largely controlled by the changes in local configuration needed to accommodate the different binding requirements of the different forms. For all sites, the overall reaction involves SQs as paramagnetic intermediates.

Our focus is on use of modern, high-resolution EPR spectroscopy to explore the catalytic domains trapped in the state with the intermediate semiquinone (SQ) bound. The catalytic sites we propose to study, - the QA and QB-sites of the reaction center, the Qi-site of the bc1 complex, and the QH-site of the bo3 quinol oxidase, - all operate using ubiquinone, but have different electron transfer partners, and different operating potentials. EPR techniques probe interactions between the electron spin of SQ and local magnetic nuclei. They thus provide direct information about spatial and electronic structure of the quinone 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. It is known that the local environment modifies the electronic state of the SQ in each protein, producing an asymmetric distribution of the unpaired electron spin density. However, there is no complete quantitative characterization of this influence. Such knowledge is crucial for detailed understanding of electron transfer and redox properties of the SQ states, and a comparison in different proteins will show which residues and how define the mechanism and the proton pathway.

In addition, elucidation of the design requirements for efficient catalysis of a lipid-bound substrate will provide important information for a more general understanding of how membrane proteins interact with substrates, metabolites, hormones, inhibitors and other effectors reacting from the lipid phase. This work has an obvious importance in pharmacology and agronomy, with immediate benefits in design of therapeutic, fungicidal, herbicidal, or insecticidal reagents that act as specific inhibitors by mimicking quinones.

Investigations into the Metabolic Diversity of Microorganisms as Part of Microbial Diversity

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Funding:	$30,000

In this project, we received five years of continued support from the Department of Energy to serve as partial funding for the Marine Biological Laboratory summer course entitled “Microbial Diversity” – a course recognized internationally as an exceptional opportunity to learn and explore the diversity of the microbial world. This project comes at a time when the pace of discovery in microbial diversity/ecology is accelerating because of the application of novel culture-independent technologies, including genomics and single cell techniques, to microbial populations. These studies, coupled with classic and modern culture techniques, are revealing hitherto unknown diversity of microorganisms and metabolisms, many of which are important to DOE missions including bioenergy, carbon cycling, environmental remediation, and microbial genomics. Moreover, these findings are expanding our understanding of biological diversity and the functioning of the biosphere.

This course is an intensive 6.5-week lecture and laboratory-based experience designed for graduate students, postdoctoral fellows, and established investigators, with the goal of educating the next generation of microbiologists so that they can take advantage of the incredible metabolic and evolutionary diversity of microbes as a means of generating fundamental and applied knowledge. The lecture component consists of lectures by staff and world-renowned guest lecturers, as well as minisymposia on current topics of interest in the areas of microbial diversity, genomics, and ecology. The laboratory component of the course takes advantage of the diverse marine, freshwater, and terrestrial natural habitats found near Woods Hole. Participants learn both classical and contemporary methods to cultivate, isolate, and characterize microbes, including strict anaerobes, such as methanogenic archaea and anoxygenic phototrophs. Moreover, they learn contemporary culture-independent techniques, including 16S rRNA gene based technologies, fluorescence in-situ hybridization (FISH), and other microscopic techniques, and genomic and phylogenetic analyses. For the second half of the course, the students use the techniques and concepts learned in the first part to carry out self-originated projects, many of which have led to publications or subsequent research. This course gives students the opportunity, seldom available at their home institutions, to use state-of-the art equipment, to meet and interact with leading researchers in microbiology, and leaves them with a new appreciation of and enthusiasm about microbial diversity.

The present course directors have chosen the theme of single cell techniques applied to natural microbial communities as a novel area to incorporate into the course during the next five years. These include novel technologies for cell separation and sorting, genome amplification from single cells, and the use of Nano-SIMS (secondary ion mass spectroscopy) techniques to examine assimilation of carbon and nitrogen from isotopically labeled substrates into single cells. These techniques promise to finally give microbiologists the ability to study individual organisms in their native environments. Besides lectures and minisymposia on single cell techniques, we will take advantage of a Zeiss laser microdissection workstation to isolate single cells of morphologically distinct uncultured organisms for subsequent genome amplification and analysis.

The MBL Microbial Diversity summer course has a reputation for excellence, and testimonials from many students who have taken it and gone on to successful careers have described it as a life-changing experience. The course's support from DOE maintains this excellence and to continue to move into new and exciting research areas in this fast moving and important field.

Integrating Cation Transport and pH Across Endomembranes With the Secretory System

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Funding:	$160,000

A long-range goal is to understand how plants regulate cation and pH homeostasis of intracellular compartments which form the dynamic endomembrane system of all eukaryote cells. Emerging evidence indicates that distinct physico-chemical environment of endomembrane compartments is important for protein sorting, membrane trafficking, osmoregulation, signaling and possibly the synthesis and remodeling of plant cell walls. However, specific transporters involved in altering ion balance, pH or both of intracellular compartments in plant cells are poorly understood. We 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 which are also localized to endomembranes. Arabidopsis CHX20, preferentially expressed in guard cells, is important for stomatal opening, and two other CHXs affect the guidance of pollen tubes, whereas the functions of four AtCHXs in roots are not well-defined. Based on localization and mutant analyses, we hypothesize that CHXs modulate the ion balance, pH or both in micro-regions of endoplasmic reticulum, endosomes and prevacuolar compartment (PVC), and so affect signaling and membrane trafficking resulting in altered osmoregulation in guard cells and polar tip growth of pollen tubes. To test this idea we are determining (1) the transport mode of CHX as a channel or exchanger; (2) the regulatory role of hydrophilic carboxyl domain 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 several uncharacterized CHX proteins in plant cells. The dynamic endomembrane of plant cells is integral to cytokinesis, cell expansion, defense, and cell wall formation, thus these studies are directly relevant to the mission of DOE and to a better understanding of determinants that enhance plant biomass and tolerance to abiotic stress.

Cellulose and the Control of Growth Anisotropy

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Funding:	$170,000

Plant cell walls are tough and strong, characteristics that give plants mechanical integrity and give humanity durable and flexible wood and fiber. In large measure, cell walls owe their strength to cellulose microfibrils, long polymers of glucose associating into partly crystalline, highly ordered arrays. The PI's previous work has helped us understand how the cell aligns microfibrils in a specific direction and how the direction of alignment governs expansion. However, cellulose synthesis itself is still poorly understood.

In this project, the PI is taking advantage of the new model plant, Brachypodium distachyon. The project objectives are to accomplish the following specific aims:

(1) Isolate and characterize root morphology mutants in brachypodium.

(2) Characterize variability in brachypodium accessions for root morphology and cellulose synthesis rate.

(3) Use reverse-genetic approaches to study the function of brachypodium genes suspected to be important in cellulose synthesis.

(4) Image tagged cellulose synthase complexes in living brachypodium roots.

In arabidopsis, conditional root morphology mutants led to the identification of the genes active in cellulose synthesis, including subunits of the synthesizing complex (CESAs). The PI hypothesizes that the approach will recover CESA family members and also will identify novel genes important for cellulose synthesis and morphogenesis in grasses. The second aim assesses the variability in root morphology and cellulose synthesis present among brachypodium accessions, and in their segregating populations, determining to what extent these characters vary as part of adaptation and potentially revealing the genetic basis. The third aim targets known genes and is testing their function in the grass by means of reducing their expression with RNA interference. The final aim is to image CESA motility in living roots by fusing a fluorescent reporter to a CESA protein, thereby allowing the velocity of cellulose synthase movement to be measured in the plant. The PI hypothesizes that the rate of movement will be influenced by microtubules, elements long thought to influence the synthesis of cellulose but through mechanisms that are still unknown.

This project studies cellulose synthesis in 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 fuel. Grasses have a different kind of cell wall than other angiosperms, and therefore cellulose synthesis and its regulation in brachypodium probably differs from that of arabidopsis, the species in which almost all of the recent discoveries about cellulose synthesis have been made. Brachypodium is a useful model grass because it is easy to handle and also because it is a temperate species and more closely related to potential biofuel crops than is rice. Focusing on cellulose, which constitutes about one third of plant biomass, the results are likely to be useful for applied efforts to improve grass crops and biofuel feedstock.

Hsp100/ClpB Chaperone Function and Mechanism

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Funding: $170,000

High temperature stress can severely limit crop productivity, particularly at critical stages of plant development. We have established that a specific cytosolic heat shock protein, Hsp101, is essential for the ability of plants to survive high temperature stress. Hsp101 is a member of the Hsp100/ClpB chaperone proteins, which are hexameric ATPases believed to function in disaggregation of denatured proteins. Significantly, plants are the only higher eukaryotes known to express this type of chaperone, indicating studies of Hsp101 should lead novel insights into mechanisms of stress tolerance. We are using genetic and molecular approaches to investigate Hsp100/ClpB proteins, including studies of both cytosolic Hsp101 and chloroplastic ClpB-p, in the model plant Arabidopsis thaliana. The ultimate goal is to define mechanistically how these chaperones influence plant growth, development, stress tolerance and productivity.

In one approach we have isolated extragenic suppressors of an Hsp101 mutant in Arabidopsis in order to define essential substrates or partner proteins of Hsp101, and as a way to uncover components of other mechanisms required for thermotolerance. We have isolated two alleles of a suppressor mutant, named shot1 (suppressor of hot1). Importantly, shot1 mutants suppress other heat sensitive mutants and are more resistant to heat than wild type plants. Therefore, the absence of Shot1 function must prevent basic damage that occurs during heat stress, reducing the need for repair functions and resulting in more stress resistant plants. We have now shown that the shot1 mutant have dramatically reduced production of reactive oxygen species (ROS) during heat stress. This result suggests that either Hsp101 facilitates repair of oxidative stress damage, or that in the absence of oxidative damage, Hsp101 function is no longer essential. This relationship of Hsp101 to oxidative stress was previously unknown. Shot1 mutants also show increased levels of mitochondrial and cytosolic Hsp70 chaperones, but not Hsp101, as determined by both microarray and western analysis. Increased levels of specific chaperones may also contribute to enhanced heat tolerance of the shot1 mutants.

Shot1 belongs to a family of 34 genes in Arabidopsis, almost all of which are predicted to be chloroplast or mitochondrial-localized, called mitochondrial transcription termination factor-related proteins (mTERFs). We hypothesize that plant mTERF proteins are a large family of understudied regulators of organelle gene expression. Alterations of nuclear gene expression in shot1 also suggest that the nucleus is responding to altered organelle function. If we can understand the mechanism by which heat stress and oxidative stress are reduced in shot1, it may be possible to prevent or reduce this type of stress in plants.

In a biochemical approach toward understanding Hsp101 function we have created plants that express affinity-tagged Hsp101 in the background of a null mutation. Initial pull-down experiments have recovered Hsp70 specifically associated with Hsp101, as well as some components of the proteasome. These are very exciting results that may link Hsp101 to regulated protein degradation. We are working towards validating these interactions.

In other efforts we have three other extragenic suppressors of Hsp101 isolated and genetically characterized with mapping populations in hand. We have Hsp101:GFP translational fusions to study localization of Hsp101 and also truncated Hsp101 mutants to investigate structural requirements for Hsp101 activity. For further studies of shot1, we have generated affinity-tagged plants for this protein as well.

Interdisciplinary Research and Related Training Program in the Plant Sciences

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Funding:	$4,200,000

Plants are the major energy transducers in the biosphere, using solar energy to convert carbon dioxide and water into chemical energy and biomass that humans use for food, fiber, pharmaceuticals and fuel. The mission of the PRL is to conduct basic plant biology research to better understand this energy conversion and to train graduate students and postdoctoral associates in this area of science. To this end, the individual research projects conducted by the PRL faculty focus on three areas germane to energy capture, flow, and deposition: (1) the biogenesis, biochemistry, and biophysics of cellular energy systems (Brandizzi, Hu, Keegstra/Froehlich, Kramer, Montgomery, and Wolk); (2) the biosynthesis and function of plant cell walls (Keegstra and Walton); and (3) the interactions of photosynthetic organisms with the environment (He, Howe, Kramer, Montgomery, and Thomashow). The research outlined in this renewal proposal advances these fundamental lines of investigation.

In addition to the individual faculty projects, we have instigated a major research initiative, the Plant BioEnergy Network—PlaNet—project. The long-term goal of this group project is to develop a deep understanding of the regulatory, biochemical, and metabolic networks that govern energy flow within photosynthetic organisms. Like all previous group projects, PlaNet is a collaborative research effort that incorporates the research interests and expertise of the current PRL faculty. However, unlike previous group projects, the PlaNet project also provides a rubric shaping the nature of future faculty hires, and the investment of significant internal funding. As outlined in our proposal, our specific goals for the coming three years focus on determining the regulatory networks that impart down-regulation of photosynthesis-associated genes in response to biotic and abiotic stresses, and photosynthetic acclimation to rapidly fluctuating environmental conditions. To address these questions, we will develop novel high-throughput “phenomics” technology—the Photosynthetic Phenomics Array (PPA). As envisioned, the PPA facility will not only provide a powerful resource for use in our own proposed research, but will also provide a major new resource for the scientific community studying photosynthesis.

Structure, Function, and Regulation of the Enzymes in the Starch Biosynthetic Pathway

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Funding: $160,000

Starch, after cellulose, is the most abundant polysaccharide in nature and is the major reserve polysaccharide in green plants. It is the primary source of caloric intake in humans and is becoming increasingly important as a renewable industrial biomaterial. The amount of starch harvested worldwide exceeds 109 tons per year. Around 2 x 107 tons of starch is used exclusively in industrial applications and this number is expected to rise as renewable sources replace petroleum-based sources of various materials. Significant interest is now focused on strategies for altering both the quantity and properties of starch from various crops. For example, there is acute interest in producing starches with high amylose content because it is more resistant to digestion. Such resistant starches have been shown to have positive health effects and are thought to contribute to the health effects of a high fiber diet. Modification of the starch biosynthetic enzymes provides a proven and fertile avenue for the achievement of these goals. Starch is a polymeric material consisting of a-1,4-linked glucose units and a-1,6 linkages that serve as branch points for the polymer. Starch granules contain two types of glucose polymers, amylose which consists almost exclusively of linear, a-1,4-linked polymers, and amylopectin which consists of highly branched polymers. The formation of a mature starch granule is a complex process, but it absolutely requires the three starch biosynthetic enzymes, ADP-glucose pyrophosphorylase, starch synthase and starch branching enzyme. The latter two enzymes create the primary a-1,4-linked glucose units and a-1,6 branch points respectively. Though the biochemical pathway for starch production is identical in all plants, the starch produced is unique to each plant species. Even within the same plant species, distinct starch types are produced in different organs. It is clear from a number of studies that these differences are largely due to the relative activities and specificities of the starch biosynthetic enzymes.

Our overarching goal is to begin to delineate in molecular detail the structure, mechanisms, specificity and regulation of the enzymes that make up the pathway for starch and glycogen biosynthesis in bacteria and plants, respectively. This knowledge will enable the rational redesign of these enzymes to both increase starch production and to alter the properties of starch. We are currently focusing our interest in understanding how these enzymes recognize and react with the developing glucan in the starch granule. To this end we have produced a number of glucan polymer-bound synthase and branching enzyme structures to understand the complex interplay between the enzymes and this large polymer. We will now use this structural information to design and carryout experiments to determine the role these interacting surfaces play in the specificity and activity of these enzymes. This will provide the insights necessary to begin tailoring these enzymes' activities to produce species that produce more useful and healthy variants of starch.

Enzymology of Methanogenesis: Mechanism of Methyl-Coenzyme M Reductase

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Funding:	$205,000

Methanogens are masters of CO_2 reduction. They conserve energy by coupling the reduction of CO_2 to CH_4, the primary constituent of natural gas, which accounts for 22 percent of the energy consumption of the U.S. Methane is considered a clean fuel because it emits less sulfur, carbon, and nitrogen than coal or oil, and leaves little ash. Methanogens produce one billion tons of methane per year and are responsible for more than 90% of Earth's atmospheric methane, the balance being generated by geochemical reactions. The goal of the research described in this proposal is to determine the enzymatic mechanism of methyl-CoM reductase (MCR), the key enzyme in methane synthesis. Uncovering the mechanistic and molecular details of how methane is formed is critical since it is an important fuel and the second most prevalent greenhouse gas.

MCR from methanogenic archaea catalyzes the terminal step in the biological synthesis of methane. Using coenzyme B (HSCoB) as the two-electron donor, MCR reduces methyl-coenzyme M to methane. Two catalytic mechanisms have been proposed for methane synthesis: one involves an organometallic methyl-Ni(III) intermediate, while the other includes a methyl radical. We are characterizing the Methanothermobacter marburgenesis MCR to elucidate the mechanism of methane formation. We have determined the X-ray crystal structure of the methyl-Ni species and determined structures of the complexes of MCR with HSCoB and several analogs. We have also trapped organometallic and radical intermediates formed during the reaction of methyl-SCoM with HSCoB6. We discovered that CO efficiently and rapidly activates MCR in vivo and propose a pathway for the cellular activation of MCR by H_2 or CO (manuscript in preparation). Finally, we have implemented the genetic system developed in Metcalf's laboratory, expressed the well-characterized MCR from M. marburgensis in M. acetivorans, purified the active enzyme and generated several MCR variants opening the door for mutagenesis studies of the key enzyme in methanogenesis. However, the challenge is to generate large quantities of the active enzyme and variants for characterization.

The Role of Phosphoinositides in Polarized Secretion of Cell Wall Components in Arabidopsis Root Hair Cells

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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. We have examined how the RabA4b effector protein, PI-4Kß1, and RHD4 function to regulate PI-4P levels during polar membrane trafficking in tip-growing cells. Specifically, we have examined how loss of these components affects accumulation and dynamics of PI-4P in root hair tips utilizing a PI-4P biosensor protein, EYFP-hFAPP1 combined with fluorescent recovery after photobleaching (FRAP) methods. In addition, using yeast two-hybrid screening methods we have identified the potential interaction of RHD4 with a calmodulin-like protein, TCH3. Second, we have examined how two classes of cell wall synthase proteins are delivered to sites of cell wall synthesis in root hair cells. From these investigations we have shown that cellulose-like polysaccharides are indeed synthesized and deposited in the tips of growing root hair cells, but that the established class of cellulose synthases, the CESA proteins, are not targeting these cellular domains and presumably are not responsible for synthesis of cellulose in the tips of these cells. Instead we have uncovered novel roles for a class of related cell wall synthases, CSLD proteins, during cell wall deposition in tip-growing root hair cells. Finally, to identify novel components which regulate polarized accumulation of RabA4b-labeled compartments in A. thaliana root hairs, we have isolated and characterized several temperature-sensitive root hair growth mutants, which we have termed loss of tip-localization (ltl) mutants. We have subsequently identified the mutated genes in three of these temperature-sensitive ltl mutants. The ltl1-1 mutation was found in a gene involved in proline biosynthesis, suggesting synthesis and accumulation of this amino acid is particularly important during the rapid expansion that occurs during root hair cell growth. Additionally, we have mapped the mutations of two additional ltl mutants (ltl2-1 and ltl2-2) and determined that they contain mutations in the same gene. Both mutants contain the same amino acid substitution in the extracellular lectin-like domain of a previously characterized receptor-like kinase, FERONIA (FER). FER, along with two other closely related receptor-like kinases THESEUS (THE) and HERACLES (HER), are all implicated in sensing and regulation of cell wall integrity. Our identification of a new temperature-sensitive allele in the extracellular lectin-like domain of FER will facilitate our understanding of how these proteins interact with cell wall polysaccharides, and how this interaction results in cell wall integrity sensing.

Two-Dimensional Electronic Spectroscopy of Light-Harvesting Complexes

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In photosynthesis, light energy is gathered by antenna proteins and transferred with almost 100% quantum efficiency to the reaction centers where it is converted to stable charge separation. The photosystem II complex (PSII) is the heart of oxygenic photosynthesis; it is unique among all biological systems in its ability to use this charge separation to split water. This proposal focuses on key deficits in our current understanding of the PSII reaction center (PSII RC); the central complex that converts solar energy into stable charge separation. Understanding the PSII RC's design principles has importance for both fundamental and applied sciences wishing to mimic its remarkable properties. We outline a series of experiments aimed at addressing 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?

The proposed experiments build on our previous work in which we developed a simple approach to two-dimensional electronic spectroscopy (2DES) that enables a direct view of electronic couplings and energy and charge transfer processes over a broad range of frequencies with ultrafast time resolution. In addition to using 2DES to study the PSII RC we propose to develop two new variants of 2DES to provide enhanced structural information about the excited states of the PSII RC and facilitate the identification of charge transfer processes. We propose applying the combined tools to address the above questions in isolated PSII RCs from spinach and in larger PSII complexes containing light-harvesting antennae. We also propose comparison studies of the unique PSII RC of Acaryochloris marina that employs chlorophyll d instead of chlorophyll a as its dominant pigment. The modified site energies of this system give it a different excitonic structure and alter the driving force for primary charge separation, allowing rigorous tests of our understanding of the PSII RC.

These combined studies on the PSII RC address the fundamental structure-function relationship in this important system to meet the Grand Challenge of elucidating the design principles used by nature to converting sunlight into chemical energy. The proposed studies will provide experimental feedback for refining models of energy and charge transfer in the PSII RC, and will push the development of new methods for simulating 2DES spectra and refining electronic structure. The new experimental tools will be widely applicable to artificial light-harvesting systems, providing information about the temporal dynamics and mechanisms of electronic energy transfer and charge separation, giving important experimental feedback for improving their design.

Functional Analysis of Plant Sucrose Transporters

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Proton-coupled sucrose uptake transporters (SUTs) are involved in the long-distance transport of sucrose. They function to load sucrose into the phloem (vascular tissue) and in uptake of sucrose into sink tissue such as seeds and flowers. SUTs are integral membrane proteins localized in the plasma membrane and vacuolar membrane and are encoded by small gene families in angiosperms and can be separated into type I, II and III based on phylogeny. In the past several years we have analyzed the biochemical transport function of representative SUTs from eudicots and monocots to determine their physiological functions, their range of substrate specificity and substrate affinity. In the current project we are investigating the structural basis for differences in transport activity that exist between SUTs of different type. We are using a number of approaches, including structural modeling, mutagenesis, electrophysiology, and plant mutant complementation, to investigate the roles that specific amino acid positions in SUT proteins have in substrate binding and transport. This information will be important for future efforts to engineer efficient carbohydrate transport to harvested organs in crop plants.

Functional Genomics Analysis of Plant Resistance to Pathogens: Impact of the Cell Wall

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There is great interest in the conversion of plant biomass to ethanol or other liquid fuels through fermentation. Prior to fermentation, the biomass must be converted to fermentable sugars. Most of the biomass is comprised of plant cell walls, which consist of a variety of polysaccharides and other polymers including cellulose, hemicelluloses, pectins, and lignins. Some of these polymers are recalcitrant to conversion to fermentable sugars, contain non-fermentable compounds, and/or inhibit fermentation. Consequently, some ideas for biofuel production involve breeding plants with altered cell wall compositions or structures that are more amenable to fermentation. A possible drawback of this approach is that plant cell walls serve as a primary line of defense against attack by microbial pathogens. Relatively little is known about the types of cell wall alterations that affect disease resistance. In this research, we will investigate the effects of cell wall changes on disease resistance using the reference plant Arabidopsis thaliana. There are three parts to the project:

(1) Create multiply-mutant plant genotypes with more severe cell wall structure and disease phenotypes. By testing Arabidopsis mutants with altered cell walls for changes in disease susceptibility, we have already identified several changes that impact disease resistance, including changes in the amount and methylation state of pectins. Due to genetic redundancy, most mutations have modest effects on the cell wall and on disease resistance. We will combine mutations with modest effects to create genotypes with larger changes in cell wall structure and disease resistance. These multiply-mutant genotypes will provide greater power for determination of the mechanisms underlying the effects of cell wall changes on disease resistance.

(2) Determine the nature of perturbations in the plant defense system responsible for altered disease phenotypes in cell wall mutants. Some changes in cell wall composition affect disease resistance through alterations in the levels of plant hormones involved in regulation of defense responses. We will examine mutants with altered cell walls to determine whether canonical defense signaling responses are affected. As our earlier work implicates a role for changes in pectin methylesterification in plant defense, we will also monitor activity of pectin methylesterases during responses to pathogen attack.

(3) Test the hypothesis that Wall Associated Kinases (WAKs) link certain cell wall changes to activation of defense responses. WAKs are likely candidates for the mechanistic link between altered pectin composition and changes in plant defense signaling because they are transmembrane proteins that bind pectin and respond to pathogen attack. We will test for a role of WAKs in mediating changes in disease resistance due to altered pectins by monitoring WAK activity in wild-type and mutant plants during pathogen attack, and by studying the effects of increases and decreases in WAK expression on disease resistance.

The results of this work will allow prediction of the effects of proposed cell wall changes on disease resistance in bioenergy crops. Deleterious changes could then be avoided. Alternatively, strategies to compensate for such deleterious effects could be designed based on our understanding of the mechanisms underlying the effects of cell wall changes on disease resistance.

Genetics and Molecular Biology of Hydrogen Metabolism in the Sulfate-Reducing Bacteria

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Funding:	$170,000

This project had two specific aims. First was the improvement of the genetics of the sulfate-reducing bacterium, Desulfovibrio alaskensis G20 (a.k.a. Desulfovibrio desulfuricans G20) so that sequential deletions could be constructed in a single strain. Therefore, genes for possible compensatory functions could be confirmed and possibly eliminated. The second aim was to establish the functions of the two transmembrane complexes, Qmo and Dsr, in the sulfate reducing pathway of Desulfovibrio strains.

We have had no major breakthroughs in the genetics of G20. Instead we have had the privilege of accessing the random transposon library for G20 created through conjugation and sequenced by A. Deutschbauer (LBNL) and, in collaboration with him, we have created a similar transposon library for Desulfovibrio vulgaris Hildenborough for another project. In these libraries, each with over 10,000 mutants, qmoABC and dsrMKJOP were not mutated, likely because the cells were cultured by sulfate respiration. The deletion of qmoABC and a hypothetical gene downstream in Desulfovibrio vulgaris Hildenborough was only possible by selection during sulfite respiration (Zane et al., 2010). The lack of recovery of transposon mutants in these two complexes clearly indicates that these two complexes are required for growth by sulfate respiration. In contrast, transposon mutants were recovered for the Hmc, Rnf, Tmc, Qrc, and Hdr complexes as well as all hydrogenases. If compensation were possible, then mutants would have been expected.

From our studies of the G20 plasmid insertion mutant in cycA, the gene for the tetraheme Type I cytochrome c3 (TpIc3) (Rapp-Giles et al.), we have established that electrons from pyruvate do not reach sulfate but that pyruvate is apparently fermented. In addition, this mutant is unable to grow with hydrogen or formate as the source of reductant with sulfate as terminal electron acceptor. When we compared protein abundances from proteomic data (obtained in collaboration with PNNL) of G20 versus the CycA mutant growing by sulfate respiration with lactate oxidation or by pyruvate fermentation, we found that the enzymes for fumarate reduction were abundant in G20 but were undetected in the mutant. Analysis of excreted metabolites showed small amounts of succinate were generated in lactate/sulfate grown G20 but not produced by the CycA mutant. Unlike G20, the CycA mutant was also not able to grow by fumarate disproportionation. Perhaps not coincidentally, when growing with lactate/sulfate, the increase in hydrogen generated by the CycA mutant was nearly equivalent to the reductant appearing in succinate from G20. The alternatives for reduced end products from organic acid oxidation have been limited in the CycA mutant by the removal of the periplasmic cytochrome.

Transcriptomic data from the CycA mutant also show a large decrease in the expression of the genes for the fumarate reductase pathway; therefore, regulation of these genes has been altered by changes in the electron flow in this mutant. A candidate two component regulatory system was identified from the genome sequences that is located upstream of a six gene operon encoding the fumarate reductase, fumarate hydratase and a putative malic enzyme. Transposon mutants with insertions in these regulatory genes as well as the structural gene for the fumarate reductase were tested and found to be unable to grow with fumarate, confirming the involvement of these regulatory genes in fumarate reduction. A manuscript on the adaptation of G20 for growth with fumarate is in progress.

Plant Response to LCO/CO Signals

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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.

The project has two specific aims: (1) investigate the mechanism of CO recognition and translation into a cellular signal and (2) investigate the mechanism by which chitotetraose and LCO suppress plant innate immunity.

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, defining the quaternary structure of the CERK1 receptor complex, and elucidating 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 reduce innate immunity. We will investigate the mechanism by which this occurs using a variety of biochemical, genetic and molecular approaches.

Our proposal relates to target areas defined in the DOE Chemical Sciences, Geosciences and Bioscience description, specifically with regard to physical biosciences, with some relevance to photosynthetic systems. For example, it is clear that CO addition to plants induces a broad array of responses, including direct impact on photosynthesis, growth and development. Although our work does not deal directly with the molecular mechanisms of photosynthesis, the information gained from our research will increase our understanding of how stress (specifically, biotic stress) impacts this process. The research also relates to Physical Biosciences since we seek to understand the molecular mechanism of plant receptor function. The research does combine experimental and computational efforts with biochemistry and molecular biology. As part of this work, we are collaborating with two DOE supported facilities, the Complex Carbohydrate Research Center (Univ. of Georgia) and Argonne National Laboratory.

Novel Microbial Based Enzymatic CO_2 Fixation/Carboxylation Mechanisms

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Funding: $153,000

The broad, long-term goal of the proposed research is to provide insight into the mechanism of novel carboxylation reactions catalyzed by enzymes involved in bacterial alkene, ketone, and epoxide metabolism. Aliphatic alkenes as well as aromatic compounds are substrates for microsomal cytochrome P450 oxygenases. These compounds are oxygenated across double bonds to the corresponding epoxides. The epoxides formed serve as alkylating reagents that can covalently modify both proteins and nucleic acids and result in mutagenic effects. A novel bacterial pathway of the aerobic microorganism Xanthobacter autotrophicus strain Py2 has recently been described in which epoxides produced by alkene oxidation and ketones produced by the oxidation of alcohols are further metabolized to ß-keto acids. The discovery of the pathway was facilitated by the ability of the organism to use aliphatic alkenes, epoxides, and ketones as sole sources of carbon and energy in spite of the toxicity of these compounds. 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. Epoxide metabolism has been shown to utilize coenzyme M, a coenzyme that had previously been thought only to be found in methanogenic bacteria. The main focus and aims of this proposal involve providing the structural basis for the mechanistic understanding of the reactions catalyzed by 2-ketopropyl coenzyme M oxidoreductase/carboxylase and acetone carboxylase, the terminal steps in the convergent pathways of alkene and ketone metabolism in Xanthobacter autotrophicus. 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 analogs and mechanism base inhibitors to ascertain information concerning the biochemical mechanisms of enzyme catalyzed reactions.

Role of HydF in Hydrogenase Maturation

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Funding: $185,000

The overall goal of this project is to advance our understanding of the mechanism of H-cluster assembly through the use of physical biochemical approaches to characterize key intermediates on the scaffold protein HydF. To further explore the role of HydF as well as the progression of steps in H-cluster maturation, we have initiated a series of experiments designed to probe how the nature of the iron-sulfur clusters bound to HydF changes as a function of changes in expression conditions. We have spectroscopically characterized HydF purified from strains where HydF was expressed with each of the radical AdoMet enzymes individually, and where the growth medium was supplemented with known or putative substrates for the radical AdoMet enzymes. We have observed distinct changes in the UV-visible and EPR spectroscopic properties depending on the expression conditions of HydF, that suggest to us that the H-cluster precursor on HydF is assembled in an ordered fashion with one radical AdoMet enzyme acting first to modify a cluster on HydF, followed by the other radical AdoMet enzyme providing the final ligands. Characterization of these presumably partially assembled H-cluster precursors on HydF by use of FTIR spectroscopy is ongoing. We have also pursued FTIR characterization of the individual maturases HydE and HydG. In order to investigate whether the CO synthesized by HydG bound to iron on the HydG protein, we used photolysis to look for the loss of Fe-CO linkages, similar to the way we have studied nitrogenase CO complexes. So far, this has not been successful. We also tried to observe Fe-CO and/or Fe-CN bond formation by a solution experiment at room temperature. The results here are intriguing, however data is still being processed. Finally, we have used low temperature photolysis to quantitate the amount of CO produced by the HydG system, by first trapping the CO on deoxyhemoglobin. We observed clean photolysis of CO-hemoglobin, and using known extinction coefficients, calculated that 27 micromoles of CO were produced.

P-type ATPases in Plants- Role of Lipid Flippases in Membrane Biogenesis

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The long-range objectives of the proposed research 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 at least one unusual subfamily (P4-type, or ALAs in Arabidopsis) that appear to flip lipids from one side of a membrane bilayer to the other. These “flippases” can be subdivided into 5 separate subgroups that are conserved in a comparison between rice (10 isoforms) and Arabidopsis (12 ALA isoforms). Their biochemical activities are thought 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.

The focus of the proposed research is on a comparison of 3 subgroups of ALAs. Aim 1 is to evaluate the influence of ALAs on the lipid composition of plant cells. Aim 2 is to initiate a genetic investigation to test whether ALAs require a putative beta-subunit for their biological functions. Aim 3 is to explore a strategy to create novel lipid storage organelles by manipulating the activities of lipid flippases. These aims are designed to provide novel and fundamental insights into an unusual subfamily of P-Type ATPases.

The primary DOE Mission-related goal is to explore the potential of using lipid flippases to create novel lipid storage organelles. These lipids could then be harvested as a feedstock for the production of biofuels.

Nanotube-Supported Phospholipid Bilayers

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Substrate-supported lipid bilayers serve many purposes: from acting as versatile biophysical models of cellular membranes to biotechnological applications such as the stabilization of membrane proteins in functional conformations for drug screening. While chemical composition of cellular membranes and their structural organization such as local shape/curvature are known to be exceptionally complex, the model substrate-supported bilayers are typically formed from just one or a mixture of a few phospholipids over substrates with planar geometry. However, spontaneous lipid bilayer bending and related curvature are now being recognized as an essential mechanism associated with many cellular functions. Specifically, experimental observations indicate that tubular vesicles of just 50 to 100 nm in diameter are commonly formed within the Golgi body and also between the endoplasmic reticulum and the Golgi.

In this DOE-funded project we are developing lipid nanotube arrays as a novel type of substrate-supported lipid bilayers with tunable curvature radius ranging from ca. 40 to 250 nm. These lipid bilayers are formed by self-assembly inside cylindrical nanopores of anodic aluminum oxide (AAO) and have nanotubular geometry. These systems have essentially no restrictions on the lipid composition and afford new opportunities for membrane biochip technology and biophysical studies of membrane proteins including those involved in biological energy transduction. The main advantages of the lipid nanotubes are (1) long-term stability of the lipid structures over the period of several months in liquid state and even longer when frozen, (2) accessibility of either one or both bilayer leaflets and the corresponding surfaces of integral membrane proteins to solvents and soluble small molecules, (3) at least a 1000-fold gain in the bilayer surface area over similarly sized planar substrate chips ligands, and (4) a high degree of macroscopic alignment for lipids and membrane proteins. The latter property is an essential prerequisite for structure-function studies of membrane proteins by solid-state (ss) NMR and is also helpful for obtaining long-distance constraints by spin-labeling DEER method.

During the current funding period, we are employing lipid nanotube technology to the following membrane protein projects: (1) incorporation of a functional photosynthetic reaction center (RC) protein from the purple bacterium Rhodobacter Sphaeroides into lipid nanotube arrays and demonstrating protein stability in excess of 90% over the period of 2 months; (2) the use of lipid nanotube array method to align membrane peptides and proteins, such as WALP and Pf1 coat protein, in lipid bilayers of various compositions and comparison of ssNMR results on protein structure with those obtained for bicelle samples; and (3) an application of lipid nanotube array technology for measuring long distance constraints in membrane protein systems by spin-labeling DEER method.

In conclusion, lipid nanotube arrays represent a versatile bilayer mimetics suitable for structure-function studies of membrane proteins and protein-lipid interactions by magnetic resonance methods.

Pathogen Virulence Factors as Unique Probes of Plant Cell Structure and Function

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We study how plant cellular machines are disrupted, usurped and modified by plant pathogen virulence factors. Of particular interest to BES and 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 siphoning plant energy to their benefit and to the detriment of their plant hosts. We use structural biology and genetics/genomics to identify large suites of pathogen virulence factors and to ascribe putative function to these via homology modeling and by solving the crystal structures if possible. We have successfully described nearly the entire repertoire of virulence factors of the type III effector class for one genus of bacterial pathogens, Pseudomonas syringae. We have used structural biology to drive mutational analysis to provide a detailed mechanistic glimpse into how one of these effectors, called AvrB, modulates activity of a host regulator of immune responses called RIN4 and how this modulation results in successful plant immune function. We have used structural homology and structure determination to drive the identification of two more type III effectors. One, HopAF1 is a deamidase that we think now manipulates production of the plant defense hormone ethylene and the second, HopB1 is a novel structure that we think has activity in scavenging host tetrapyrole derivatives. We have discovered a unique plant disease resistance gene that recognizes the presence of HopBA1 and its structure is a target for our next funding phase.

This project is a fruitful collaboration between a genetics lab and a structural biology lab. We trained three students and one post-doctoral fellow in part or in whole during this round of funding.

Sugar Sensing in Arabidopsis via AtRGS1

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Funding:	$165,000

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.

Heterotrimeric guanine nucleotide–binding protein (i.e., G protein, from above)-coupled receptors (GPCRs) in animals initiate signaling by activating the alpha-subunits of G proteins; however, the plant Arabidopsis thaliana lacks canonical GPCRs and instead employs a distinct mechanism of G protein activation. Most importantly, nucleotide exchange by the plant Galpha subunit, AtGPA1, is more than 100-fold faster than nucleotide exchange of the fastest known G protein in animals leaving us with the paradox on how plants control G protein activation. To investigate how the plant G protein alpha-subunit AtGPA1 becomes activated, we determined its crystal structure. AtGPA1 is structurally similar to animal Galpha proteins, but our crystallographic and biophysical studies revealed that it had distinct properties. Notably, the helical domain of AtGPA1 displayed pronounced intrinsic disorder and a tendency to disengage from the Ras domain. Domain substitution experiments showed that the helical domain of AtGPA1 was necessary for self-activation and sufficient to confer self-activation to an animal G protein alpha-subunit. These findings reveal a mechanism for G protein activation in Arabidopsis that is distinct from the well-established mechanism found in animals. This work also provided the first evidence of a function of the helical domain of Galpha subunits.

Proteins with nearly identical crystal structures such as those we showed for AtGPA1 (discussed above) and the human protein, Galpha-i1, can still have activation rates that vary over multiple orders of magnitude but there was no clue as to how this could occur. Therefore, we employed molecular dynamic (MD) simulations to investigate the role of atomic motion in conferring distinct activation properties to these two Galpha proteins, AtGPA1 and Galpha-i1. We found that motions in these proteins vary greatly in type and frequency. Whereas fluctuations are largest in the Ras-like domain of Galpha-i1, motion is greatest in helices A and B from the helical domain of GPA1. Using protein chimeras, we showed further that helix A from AtGPA1 is sufficient to confer the rapid nucleotide exchange property to Galpha-i1. This rate enhancement occurs despite a 10 angstrom distance between the substituted helix and the nucleotide. These results greatly altered our understanding of G protein activation.

To better understand the cycle of G protein activation and inactivation in plants, we purified and reconstituted AtGPA1, full length AtRGS1 (Arabidopsis Regulator of G signaling protein, an unusual 7 transmembrane receptor like protein) and two putative Gbeta-gamma dimers. We show that the Arabidopsis Galpha protein binds to its cognate Gbeta-gamma dimer directly and in a nucleotide-dependent manner. Although animal Gbeta-gamma dimers inhibit GTP binding to the Galpha subunit, AtGPA1 retains fast activation in the presence of its cognate Gbeta-gamma dimer. We show further that the full length AtRGS1 protein accelerates GTP hydrolysis and thereby counteracts the fast nucleotide exchange rate of AtGPA1. Finally we show that AtGPA1 is less stable in complex with GDP than in complex with GTP or the Gbeta-gamma dimer. Molecular dynamics simulations and biophysical studies reveal that altered stability is likely due to increased dynamic motion in the N-terminal alpha-helix and Switch II of AtGPA1. Thus despite profound differences in the mechanisms of activation, the Arabidopsis G protein is readily inactivated by its cognate RGS protein and forms a stable, GDP-bound, heterotrimeric complex similar to that found in animals.

The heterotrimeric G protein complex provides signal amplification and target specificity for sugar signal transduction. The Arabidopsis Gbeta subunit of this complex (AGB1) can interact with and modulate the activity of cytoplasmic proteins. The specificity resides in the structure of the interface between AGB1 and its targets. Mutations made on the surface of AGB1, which were deduced from a comparative evolutionary approach, enabled dissection of various AGB1-dependent physiological functions, including the efficiency of photosynthesis and disease resistance. Analysis of the capacity of these mutants to complement well-established phenotypes of Gbeta-null mutants revealed AGB1 residues critical for generic effector binding and those binding to effectors involved in specific biological processes. These findings provide new information to direct finely-tuned engineering of crop yield and traits, especially those that provide the US with more energy, food, and fiber with fewer agronomic inputs.

Transmethylation Reactions During Methylotrophic Methanogenesis in Methanogenic Archaea

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Our DOE sponsored project has focused on how methanogens produce methane from methylated compounds, such as monomethylamine (MMA), dimethylamine (DMA), or trimethylamine (TMA). This work led to the discovery of three distinct methyltransferases, one for each methylamine. Each methyltransferase methylates a corrinoid cofactor bound to a distinct 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 possesses an in-frame amber codon that we have shown corresponds to pyrrolysine, the 22nd amino acid. As a result, we have focused on pyrrolysine function as key to the understanding of how methanogenesis is initiated from methylamines. In the current grant period (starting 8/1/10) our goals have included the function of pyrrolysine in MttB, the trimethylamine methyltransferase. We aim to replace the pyrrolysine with several other residues, as well as to replace surrounding residues, and determine the effects on activity. Additionally, we are better characterizing the reaction catalyzed by RamA. DOE support is also being used to partially support a project in which we delineated the biosynthetic pathway of pyrrolysine, and another in which we have defined the tRNAPyl binding domain of pyrrolysyl-tRNA synthetase, PylS. PylS is essential for insertion of pyrrolysine into methyltransferases during translation.

The Structure of Pectins

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Pectin is the most abundant polysaccharide in primary plant cell walls of dicots and has a very complex structure. The function of pectin in cell walls is not well understood, but modifications of the structure occur naturally during plant development and some mutations leading to modifications in structure have severe phenotypes. Pectin is composed of four structurally distinct regions each of which has its own complexity and may or may not be linked to each other. About half of the xyloglucan in cell walls is covalently linked to pectin and there is fairly strong evidence that the cell wall protein Extensin is also covalently linked to pectin. It is our expectation that the primary plant cell wall is a covalently cross-linked network of polysaccharides (and sometimes protein) analogous to the bacterial peptidoglycan network and the glucan-mannoprotein-chitin network in yeast.

One goal of the project is to characterize the linkages between the various regions of pectin and between pectin and the other polymers. The other is to discover putative transglycosylases that form the linkages between the polymers.

To find the cross-linkages we will use cloned (monospecific) enzymes to degrade the polymers and separate out fragments which retain characteristics of two different polymers. These will then be characterized by NMR and mass spectroscopy. We have isolated and characterized oligosaccharides representing the cross-linkages between homogalacturonan and rhamnogalacturonan (RG) and between galactans and arabinans and RG during the previous grant period. It remains to be determined how xylogalacturonan and rhamnogalacturonan are linked together. We have also found that xyloglucan and RG are cross-linked via a highly branched 1-5 linked arabinan. We plan to characterize the connections between the arabinan and the xyloglucan and between the arabinan and the RG using the same fragmentation, separation, and characterization approach mentioned above.

To find the transglycosylases we are planning to develop an assay using the recently developed BlotGlyco beads. These beads are made by polymerizing an acrylamide monomer to which hydrazine is attached. The high density of hydrazide groups allows reducing sugars to covalently attach to the beads. Oligosaccharides which are putative acceptors for the transglycosylases will be attached to the beads and then exposed to protein extracts from plants and potential glycosyl donors. After an incubation period all extraneous materials can be washed away and the beads interrogated with enzymes which should release fragments of attached donor. Since the hydrazide-sugar linkage can be reversed by warm mildly acidic conditions the acceptor oligomer with a fragment of the donor should be recoverable from the beads.

Bioenergetic Aspects of Syntrophic Fatty and Aromatic Acid Metabolism

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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. During syntrophy, hydrogen or formate are produced from electrons generated in the oxidation of fatty and aromatic acids, which requires energy input by a process called reverse electron transfer. The objectives of this proposal are to (1) detect the membrane complexes involved in reverse electron transfer; (2) identify gene systems induced under growth conditions that require reverse electron transfer; (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 if *S. wolfei* and S. *aciditrophicus* have electron-bifurcating hydrogenases and formate dehydrogenases that could be used for reverse electron transfer of electrons from NADH to H_2 or formate.

We analyzed the membrane complexes of *S. wolfei* grown either fermentatively on crotonate or syntrophically on butyrate with the methanogen *Methanospirillum hungatei* JF1. Membrane complexes were electrophoretically separated using blue-native gel electrophoresis and observable bands were digested and sequenced using liquid chromatography tandem mass spectrometry. We observed at least one complex unique to syntrophic growth on butyrate. Sequence analyses showed that this complex contained butyryl-CoA dehydrogenase, electron transfer flavoprotein, an iron-sulfur (FeS) oxidoreductase, hydrogenase and ATP synthase subunits. The subunit composition suggests that the complex could function to produce hydrogen from electrons derived during butyryl-CoA oxidation, possibly driven by chemiosmotic energy. Transcriptional analysis showed that the genes encoding these peptides were upregulated during syntrophic growth on butyrate. ATP synthase complex was detected in *S. wolfei* membranes under all growth conditions. A complex potentially involved in protein translocation was detected in crotonate-grown *S. wolfei* membranes. A similar approach was done to analyze the membrane complexes of *S. aciditrophicus* involved in syntrophic benzoate and cyclohexane carboxylate metabolism compared to fermentative metabolism on crotonate. We are just beginning to analyze the mass spectral data, but so far have detected components of an ion-translocating, ferredoxin-NADH oxidoreductase in membranes of crotonate-grown *S. aciditrophicus*. Blue-native gel electrophoresis detected several unique bands when *Syntrophobacter fumaroxidans*, which syntrophically oxidizes propionate and these bands have been sent for sequencing.

The whole cell proteome of *S. wolfei* grown axenically on crotonate and syntrophically with *M. hungatei* with crotonate and butyrate was analyzed to determine proteins involved in key redox and energy conservation reactions necessary for syntrophy. Proteomic analysis identified a total of 1090 polypeptides. Thirty-four polypeptides, including a zinc-dependent dehydrogenase with a GroES domain, were detected only in syntrophically grown *S. wolfei* (e.g., in coculture with *M. hungatei* on butyrate or crotonate). Multiple systems for interspecies electron transfer and reverse electron transfer including a confurcating hydrogenase, a putative membrane-bound hydrogenase, and a novel FeS oxidoreductase thought to serve as an electron transfer flavoprotein (ETF):quinone oxidoreductase were also detected. The latter components were detected in the butyrate-induced complex discussed above. Beta-oxidation enzymes and ETF were detected in each growth condition. Under syntrophic conditions, the abundance of proteins involved in coenzyme and amino acid transport as well as metabolism increased while crotonate axenic conditions saw increased abundance in proteins involved in lipid transport and metabolism. The whole cell proteomic analysis demonstrates that *S. wolfei* expresses multiple enzyme systems for fatty acid metabolism, interspecies electron transfer, and energy conservation under all growth conditions. A unique membrane complex is induced in *S. wolfei* during syntrophic butyrate oxidation, which we hypothesize may function in hydrogen production from butyryl-CoA using chemiosmotic energy. Further biochemical studies are ongoing to test this hypothesis. Our bioenergetic study of syntrophy integrates genomic, functional genomic, and biochemical approaches to understand an essential and poorly characterized process critical for carbon cycling on the planet and will demonstrate how bacteria operate at free energy changes close to equilibrium.

Genes Needed for H_2 Production by Sulfate Reducing Bacteria

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Funding:	$220,000

In order to identify proteins involved in H_2 metabolism in Desulfovibrio desulfuricans G20, transposon insertion mutants deficient in syntrophic growth were identified and are being characterized. A screening done with G20 in a hydrogen uptake role in coculture with Syntrophomonas wolfeii identified mutants for the membrane protein complex annotated as Rnf. The G20 Rnf is homologous to proteins involved in oxidation of ferredoxin coupled to the pumping of protons or sodium ions. The electron acceptor in G20 could be NAD or it could be a sulfate reduction intermediate. The Rnf protein in G20 appears to be involved in H_2 and formate uptake, as G20 mutants will not grow on H_2 or formate. Although it is possible that Rnf could be involved in generation of NADH for biosynthesis, washed-cell experiments show that the Rnf mutants RnfA and RnfD produce very little sulfide from sulfate with H_2 or formate as a substrate, indicating that the Rnf complex must be part of a pathway for H_2 metabolism linked to sulfate reduction. Our previous efforts in this area have described a set of proteins which include Qrc that are most likely involved in H_2 uptake and H_2 production in G20. It is possible that that Rnf provides an alternative and also required mechanism of H_2 oxidation in G20 or that the Qrc system is coupled to Rnf during H_2 metabolism. We are currently identifying the specific mechanisms by which Rnf allows the cell to grow with H_2.

We have also recently identified mutants in the flhA flagellar biosynthesis gene, the fliF flagellar ring gene, and the pilA pilus assembly gene grew less than the parent strain, suggesting a role for chemotaxis or other flagellar function in syntrophy. Microscopy showed the flhA and fliF mutants to lack flagella and both flagella mutants and the pilus mutant produced considerably less biofilm than the parent strain. Recent experiments suggest that the flagella mutants grow more slowly on H_2, perhaps indicating a need for motility during H_2 growth in laboratory cultures.

The membranes of several mutants of Desulfovibrio vulgaris including a qmo (quinone membrane oxidoreductase) mutant were extracted and separated on Blue Native gels to identify large protein complexes. The qmo mutant was found to be missing several bands compared to the parental strain. These bands were identified to be the qmo protein complex as well as a complex of the qmo and APS reductase, suggesting that these two proteins operate as a multiprotein complex during H_2 oxidation. Affinity tagged genes are being used to verify this phenomenon as well as to identify other proteins that may be involved in this electron transport complex.

Molecular Mechanisms of Plant Cell Wall Loosening

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We are studying the biophysical and molecular bases of plant cell wall loosening, which is essential for plant cell growth and is connected to other developmental processes and to plant defense. Our focus in this project is on the interactions of expansin proteins with cell wall polymers, with the aim of understanding how expansins modify wall polymer interactions and structures, resulting in physical effects such as wall stress relaxation, polymer creep, and increase in surface area of the cell wall.

We are working with three groups of expansins with distinctive biological roles and biophysical actions on plant cell walls: bacterial expansins, plant ß-expansins from maize pollen, and plant a-expansins that mediate 'acid growth'. Bacterial expansins were recently discovered by virtue of their structural similarity to the maize pollen ß-expansin ZmEXPB1, whose structure we solved in 2006. They are limited in distribution to a small but diverse group of bacteria that colonize plant roots or that cause vascular wilt. Our principle interest in bacterial expansin stems from the ease with which they can be expressed and genetically manipulated in recombinant form. As a result we have recently carried out a structure-function analysis of the bacterial expansin from Bacillus subtilis, EXLX1, identifying amino acid residues crucial for cell wall binding and wall extension activity and showing that the D2 domain is the principle determinant of EXLX1 binding to cell walls.

We have produced crystals of a complex of EXLX1 and cellohexaose and obtained a (1.95 A) molecular structure which displayed an unusual feature: the ligand is sandwiched between the strip of aromatic residues in the D2 domain of two EXLX1 proteins. This unusual feature of the EXLX1:cellohexaose complex may reveal unique aspects of the wall-loosening action of expansins. We therefore are studying this crystal structure in detail to understand the nature of the interactions that give rise to sugar ring distortion and attempt to create variants of this structure with modified forms of EXLX1, different oligosaccharides, and with EXLX1 homologs from other bacteria, in an effort to test whether expansin activity and these unusual molecular features are linked together.

We will extend the lessons learned from dissection of bacterial expansins to plant expansins by a series of experiments to define ZmEXPB1 binding specificity and to make crystals of an EXPB:oligosaccharide complex. We will also attempt this with the ZmEXPB1 D2 domain, which we expect is readily expressed and correctly folded in E. coli. To overcome the current limitation in recombinant expression of a-expansins, we have planned a strategy to express a diverse set of a-expansins in E. coli lines designed to solve some of the solubility problems we have encountered in a-expansin expression. Lastly, we use high-resolution imaging and novel spectroscopy methods to investigate the location of expansins in the cell wall at the nm-scale and to characterize changes in wall structure at the nm-scale caused by expansins.

This work is relevant to energy research because plants and plant cell walls are major sources of biorenewable fuel. Our work may give critical insights into the control of plant cell growth and cell wall physical properties and potentially could inspire the development of new catalysts for disassembling the cell walls for energy and material needs by society.

New Perspectives on Acetate and One-Carbon Metabolism in the Methanoarchaea

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Carbonic anhydrases catalyze the reversible hydration of carbon dioxide to bicarbonate. Although widespread in prokaryotes of the domains Bacteria and Archaea, few have been investigated and the physiological functions are largely unknown. Carbonic anhydrases are of biotechnological interest for carbon dioxide capture and sequestration at point sources. Prokaryotes encode three independently evolved classes (alpha, beta, and gamma). The alpha-class is restricted to a few pathogens and the other two are uniformly distributed in phylogenetically and physiologically diverse species. Although widespread in prokaryotes, only three gamma-class enzymes have been biochemically characterized and the physiological functions have not been investigated. The gamma-class is prominent in anaerobic acetate-utilizing methane-producing species of the genus Methanosarcina that encode three subclasses. Enzymes from two of the subclasses, Cam and CamH from *Methanosarcina thermophila*, have been characterized and found to utilize iron in the active site which is the first example of an iron-containing carbonic anhydrase. No representative of the third subclass has been isolated, although this subclass constitutes the great majority of the gamma class. This grant application proposes to characterize gamma-class carbonic anhydrases from diverse anaerobic prokaryotes from the domains Bacteria and Archaea to broaden the understanding of this enzyme. In particular, the three subclasses present the genetically tractable acetate-utilizing methanogen *Methanosarcina acetivorans* will be investigated to extend studies of acetate and one-carbon metabolism in this species. A genetic approach will be taken to ascertain the physiological functions. It is also proposed to delve deeper into the mechanism of Cam from *M. thermophila*, the archetype of the gamma class, *via* a high resolution neutron structure and kinetic analysis of site-specific amino acid replacement variants.

Functional Analysis and Genetic Manipulation of Plant ABCB Organic Ion Transporters

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Efforts to manipulate the production of plant secondary cell walls to improve the quality of biofuel feedstocks are currently limited by an inability to regulate the transport of small molecule components out of the cell. Plant ATP Binding Cassette class B (ABCB) p-glycoproteins are a small family of plasma membrane organic molecule transporters that have become primary targets for this effort, as they can potentially be harnessed to control the export of aromatic compounds and organic acids. However, unlike promiscuous mammalian ABCBs that function in multidrug resistance, all plant ABCB proteins characterized to date exhibit relatively narrow substrate specificity. Our central hypothesis is that the domains of the ABCB proteins that we have identified as substrate docking sites and regulators of transport directionality can be altered or swapped to alter the transport characteristics of the proteins. This project is directed at manipulation of ABCB activity to ultimately produce "designer" ABC transporters that can be used to modify plant feedstock quality.

2011 FISCAL YEAR PROGRESS ON THE PROJECT

(1) Identified the basis of reversible substrate export by the class of plant ABCB transporters represented by ABCB4. Results demonstrated that ABCB4 is a substrate-activated regulator of cellular concentrations of the phytohormone auxin in the root apex and root hairs. Uptake kinetics of ABCB4 were shown to differ from the saturation kinetics of the AUX1 permease as uptake converted to efflux at threshold IAA concentrations. ABCB4 association with membranes was shown to involve hydrophobic interactions not present in exclusive exporters In heterologous systems and in planta, ABCB4 transports benzoic acid with weak affinity, but not the oxidative catabolism products oxindole-3-acetic-acid and 2-oxindole-3-acetyl-ß-D-glucose. ABCB4 mediates uptake, but not efflux, of the synthetic auxin 2,4-D in cells lacking AUX1 activity. These results suggest that 2,4-D is a non-competitive inhibitor ABCB4 and that ABCB4 is a target of 2,4-D herbicidal activity at the root surface. These results validated the placement of substrate uptake sites with non-specific substrate exclusion sites in ABCB transporter and supported the hypothesis that internal binding sites identified in modeling should be modification targets for export of cell wall components in biomass crops. Published in This work is published in *Plant Journal DOI: 10.1111/j.1365-313X.2011.04818.x.*

(2) Established that activity of ABCB19 is regulated by light and PHOT1 kinase. It was demonstrated that the photoreceptor kinase PHOTOTROPIN 1 (phot1) phosphorylates ABCB19 and inhibits its transport activity to increase auxin levels in and above the hypocotyl apex, halt vertical growth, and prime lateral fluxes that are subsequently channeled to the elongation zone by PIN-FORMED 3 (PIN3). PHOT1 association was also shown to negatively regulate interactions of ABCB19 with the FKBP chaperone TWD1, thus validating proposed regulatory domains in ABCB19 models. These results allow for differentiation of regulatory sites that govern activity versus those that also regulate protein trafficking and stability- an important distinction for engineering of ABC transporters in biofuel crops. This work is published in *PLoS Biology doi:10.1371/journal.pbio.1001076.*

(3) Models of plant ABCB transporters were reinterpreted based on new experimental data and published structural analyses of mammalian ABCB transporters. These modeling efforts clearly differentiate between the membrane xenobiotic exclusion sites and inner leaflet sites associated export of specific substrates. This work is published in *Frontiers in Plant Science* (doi not yet provided).

(4) The validity of the use of the S. pombe heterologous transport system for substrate uptake studies has been questioned, as those studies all utilized substrates that exhibit lipophilic cellular uptake under some conditions. The system was used to demonstrate the uptake characteristics of a nicotine uptake transporter from tobacco and show that the uptake did not include other related alkaloids and growth regulators. These results were compared to results from intact plants and clearly showed the transferability of uptake studies from the S. pombe system to studies of cell wall component export in planta. As a result, the system is now in use in at least four other projects funded by BES to accelerate their research. This work is published in *PNAS 10.1073/pnas.1108620108*.

Phenylpropanoid Metabolism in Arabidopsis: The Role of REF4

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The sun is the principle source of energy for our planet, and photosynthesis is the primary mechanism by which that energy is captured and stored in the form of reduced carbon. An outcome of these biochemical events is that plants represent a quantitatively important, sustainable, and carbon-neutral source of energy for humans. In order to maximize the utility of plants for this purpose, it is important that we gain control of the processes associated with energy capture and storage, including the molecular mechanisms that allocate fixed carbon to the myriad biochemical pathways in plants. One of the most significant of these is the phenylpropanoid biosynthetic pathway which leads to the deposition of lignin. Lignin is a cross-linked phenolic polymer that makes the cell walls of specialized plant cells more rigid. Its synthesis represents the single largest metabolic sink for phenylalanine in the biosphere and as such represents a huge metabolic commitment for plant metabolism. Lignin is also a significant barrier to the use of crops for livestock feed, pulp and paper production, and to the generation of cellulosic biofuels. Our objective is to push forward our basic understanding of lignin biosynthesis while simultaneously adding to our ability to engineer plant metabolism so that it can be modified for the improvement of agriculture.

Although the enzymes of lignin biosynthesis have now been identified, we know relatively little about how their expression is regulated. Several relevant transcription factors have been isolated, but it is unclear how their expression and activity dictate or contribute to the allocation of photosynthate to lignin as opposed to other plant components such as cellulose, starch, or any other sinks for reduced carbon.

We are in a unique position to explore how the amount of lignin in a plant is controlled because we have identified two novel, plant-specific proteins (REF4 and RFR1) that are components of Mediator, a large multi-protein complex that facilitates interactions between DNA-bound transcription factors and RNA polymerase II to activate or repress the expression of downstream genes. Mutants of Arabidopsis that lack REF4 and RFR1 are viable and show little in the way of developmental changes, making them a tractable system in which to examine the function of Mediator. Of particular relevance to this project is that these mutants accumulate more phenylpropanoid end products including lignin. Plants carrying a mutant dominant form of REF4 show the opposite phenotype. Thus, REF4 and RFR1 appear to be components of a system that determines the amount of carbon allocated to the phenylpropanoid biosynthetic pathway. Considering that over 108 gigatons of lignin are synthesized annually in the biosphere, these proteins are important players in the global carbon cycle and represent important new opportunities for the manipulation of lignin synthesis in plants.

To elucidate how REF4 and RFR1 function as components of Mediator we will use a robust set of experimental approaches including immunoprecipitation and yeast two-hybrid methods to determine the proteins with which REF4 and RFR1 interact in the Mediator complex. These experiments will establish which proteins are relevant to the regulation of phenylpropanoid accumulation in plants and may simultaneously identify additional proteins that are relevant to this process that were not previously known to be part of Mediator. We will then use chromatin immunoprecipitation to identify the targets of the REF4 and RFR1 proteins in the Arabidopsis genome in order to understand which genes must be altered in their expression to divert more or less carbon into the lignin biosynthetic pathway. Finally we will determine whether there are functional differences between REF4 and RFR1 by altering their relative expression levels in different tissues. By completing this entire set of experiments, we will learn how REF4 and RFR1 function to coordinate transcription of genes required for lignin deposition and gain insights into how this pathway can be manipulated for human energy needs.

Transcription Regulation of CelS and a Novel Cellulase Operon Encoding Five Clostridium Thermocellum Cellulosomal Components

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CelS is the most abundant subunit of the Clostridium thermocellum cellulosome, an extracellular multiple-enzyme complex for cell wall degradation. It is also the only exo-glucanase unambiguously identified in the cellulosome. The regulatory mechanism of its biosynthesis remains largely unknown. To determine if the celS gene is regulated through a transcription factor, we carried out the electrophoretic mobility shift assay (EMSA) using the promoter region of celS as a probe. The probe was biotinylated to facilitate immune-detection. A DNA-binding protein was detected on the -200 to-300 bp promoter region, indicating that there is a putative transcription factor binding to this region of the celS promoter.

To identify the putative transcription factor, we used affinity chromatography to fish out the protein from the cell lysate using the promoter DNA sequence as the affinity ligand. The bound proteins were eluted and their identities determined by LC/MS-MS. The candidate DNA binding proteins were cloned and expressed in E. coli, purified, and tested for their ability to bind to the promoter region of celS by EMSA. We found an AbrB-like protein, binds to the celS promoter region.

The recombinant AbrB-like protein bound to the celS promoter probe in a dose-dependent manner in EMSA. The recombinant AbrB-like protein did not bind to the xynC promoter probe. As a negative control, we also showed that another recombinant protein did not bind to the celS promoter probe. Thus the EMSA results demonstrated that the AbrB-like protein binds specifically to the celS promoter region.

To verify the AbrB-like protein is indeed responsible for the gel-shift activity of the crude cell lysate, we excised the shift-band caused by the cell lysate, eluted the protein by electro-elution, and determined the identity of the protein by LC/MS-MS. The result showed that the eluted protein is indeed the AbrB-like protein (with 57% sequence coverage by LC/MS-MS). We have thus identified the putative transcription factor that binds to the -200 to -300 bp celS promoter region. This is the first celS transcription factor identified. Further study of the function of the AbrB protein will shed light on the regulation of this important cellulosomal protein.

Imaging of Conformational Changes for Single Proteins in Solution by Suppression of Brownian Motion

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The primary objective of this research is to study and understand the behavior of individual photosynthetic antenna proteins and redox enzymes in a physiologically relevant solution environment. Single-molecule measurements have been firmly established as a cutting-edge technique for elucidating mechanistic details of biological processes; and they have found applications in the examination of enzymes, biomotors, chaperonins, and antenna proteins, just to name a few. A special aspect of our work is that we wish to avoid attaching the single biomolecules to a surface in order to prevent deleterious perturbations, while at the same time, we require that we observe each single molecule as long as possible. Our recently developed Anti-Brownian ELectrokinetic (ABEL) trap enables such studies, and we have applied this device to study a photosynthetic antenna protein, Allophycocyanin, APC, where we observed unexpected conformational- and photo-dynamics, an unprecedented observation for a solution-phase protein.

To build upon our successes with APC, we are now exploring other photosynthetic antenna proteins, in particular, the LH2 antenna from purple bacteria (provided by R. Cogdell), as well as the Fenna-Matthews-Olsen (FMO) complex (provided by R. Blankenship) and the Peridinin-Chlorophyll-Protein light-harvesting complex. In addition, we recently completed a detailed study of the dynamics of the Nitrite Reductase (NiR) redox enzyme using the ABEL trap, and we are actively exploring potential collaborations to study other enzymes involved in redox chemistry.

As we continue to investigate molecules relevant for energy collection and converstion, we are continuously enhancing the ABEL trap to improve trapping performance and thus to increase the information we can extract from each single molecule. In one effort, we developed an adaptive version of the trap which yields real-time estimates of the diffusion coefficient and the mobility of the trapped biomolecule. In another, we have begun direct measurements of the emission spectrum of single APCs in the trap, an approach which we believe will help uncover the steps in the light-driven photoconversion process that occurs.

In summary, we continue our work to both develop the ABEL trap technique and to apply the system to understand mechanisms of exciton and electron dynamics in photosynthetic antenna proteins and in redox enzymes.

Ferredoxin-Dependent Plant Metabolic Pathways

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The iron-sulfur protein ferredoxin serves as the physiological donor for many enzymes that play key roles in carbon, nitrogen and sulfur metabolism in oxygen-evolving photosynthetic organisms. Ferredoxin, which is reduced by Photosystem I in a light-dependent process, also serves as the electron donor for the thioredoxin-dependent regulation of enzymes involved in many metabolic pathways and as the electron donor in a key step in the synthesis of phytobilins – pigments involved in both light-harvesting and in signaling cascades. The proposed research is designed to elucidate the mechanisms of five enzymes that use ferredoxin as the electron donor and to discover the details of the interactions of ferredoxin with these different enzymes, all of which form protein/protein complexes with ferredoxin. Particular emphasis will be placed on site-directed mutagenesis experiments designed to characterize the substrate-binding sites of two ferredoxin-dependent enzymes, nitrite reductase and glutamate synthase. A second major area of emphasis will be the characterization of the thermodynamics of complex formation between ferredoxin and several of its target enzymes, using isothermal calorimetry.

Jasmonate Signaling and Stamen Development in Arabidopsis

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RESEARCH GOALS

Our original interest in understanding the role of jasmonate hormone (JA) in regulating the final stages of stamen and pollen development led to our discovery of the JAZ repressors, and the molecular mechanism of JA hormone action is now a second important focus of our research. Our specific goals for 2011 were to (1) identify the functions and regulatory relationships among the transcription factors involved in JA-mediated stamen maturation using mutants, dominant-negative constructs, and regulated expression of the genes encoding them and (2) employ specific assays and yeast-two-hybrid screens to identify additional transcription factors that interact with the JAZ proteins. Mutant analysis, overexpression, and dominant-negative constructs were to be used to probe the roles of these transcription factors in mediating JA responses.

RESULTS

JA hormone plays important roles in regulating the synthesis and accumulation of plant secondary products, and is also required for fertility. JASMONATE ZIM-DOMAIN (JAZ) proteins inhibit transcription factors that regulate early JA-responsive genes, and JA-induced degradation of JAZ proteins thus allows expression of these response genes. Until this year, MYC2 was the only transcription factor known to directly interact with JAZ proteins and regulate early JA responses, but the phenotype of myc2 mutants suggests that other transcription factors also activate JA responses. Yeast-two-hybrid and pulldown assays identified MYC3, MYC4 and MYC5 as additional transcription factors that interact with the JAZ repressor proteins. Although myc3 and myc4 loss-of-function mutants showed no phenotype, transgenic plants overexpressing MYC3 and MYC4 had higher levels of anthocyanin compared to the wild-type plants. In addition, roots of MYC3 overexpression plants were hypersensitive to JA. Quantitative real time RT-PCR analysis of nine JA-responsive genes revealed that eight of them were induced in MYC3 and MYC4 overexpression plants, except for a pathogen-responsive gene, PDF1.2. Similar to MYC2, MYC4 negatively regulates expression of PDF1.2. Together, these results indicate that MYC3 and MYC4 are JAZ-interacting transcription factors that regulate JA responses.

We have previously identified a series of MYB transcription factors that contribute to the development of fertile stamen and pollen during reproductive development. One of these, MYB21, is required for plant fertility – myb21 null mutants are substantially sterile. To find out if MYB21 is sufficient for male fertility in the absence of JA signaling, we expressed a MYB21 transgene in mutants deficient in JA synthesis (opr3). MYB21 expression rescued the sterile phenotype of these mutants, indicating that this transcription factor is the master regulator of the very large gen-expression cascade that is required for correct stamen and pollen development in Arabidopsis.

Lignin Biopolymer Assembly and Primary Structure: A (Bio)Chemical Characterization

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Lignins, the second most abundant biopolymers in vascular plants relative to cellulose, 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, and represent an enormous barrier to either facile conversion of biomass carbon into chemical feedstocks, to development of new pulp/paper production processes, or improved animal feedstuffs etc. Yet, the successful evolution of vascular plants appears to have largely hinged on the capability to produce lignins. They provide a most effective means to help reinforce plant cell walls in the vasculature, thereby enabling those organisms to be able to stand upright, to be able to dynamically respond to different environmental effects (including effects of wind/rain/snow and in pathogen resistance), as well as providing a conduit for water/nutrient transport in planta. There has been much debate about the nature of lignin configuration; early considerations suggested that these were 3D cross-linked polymers, randomly assembled, and thus similar to thermosets. However, various analyses of lignins in-situ, and as isolates, established they are more linear (thermoplastic) like. There is thus much need to develop new means to identify lignin polymer primary structure, as well as to much 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 their biophysical/biomechanical properties.

Using Arabidopsis and poplar, the first two plant species whose genomes were sequenced, it has become possible to systematically dissect the lignin-forming process in-situ. During this reporting period, we have differentially reduced lignin levels from near wild type/native levels to the lowest amounts yet reported. This was achieved through generation of a variety of knockouts of genes encoding the six-membered arogenate dehydratase family we discovered which produces phenylalanine. Together with employing other plant lines containing genetic modifications of various (NAC) transcription factors, and the use of laser microscopy dissection, these approaches have provided much new insight as regards both lignin primary structure and the differential processes involved in lignification in specific cell types, such as vascular bundles and fibers, respectively. Furthermore, a suite of both chemical and biophysical approaches are being developed to probe lignin polymeric structures and properties on a cell-by-cell basis. These findings are beginning to resolve the major outstanding questions of lignin complexity, and provide a basis for rational redesign of lignin's biophysical properties, and questions of lignin assembly and potential use.

The Rhizobial Nitrogen Stress Response and Effective Symbiotic Nitrogen Fixation

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The nitrogen fixing symbiosis between Sinorhizobium meliloti and alfalfa generates fixed nitrogen that allows the plants to grow without additional nitrogen fertilizer. In this way, symbiotic nitrogen fixation is an alternative to using industrially generated ammonium, which uses significant inputs of methane. The symbiotic interaction requires efficient exchange of nutrients between the symbionts. This project has been studying an unusual mutant of S. meliloti that fixes nitrogen at or above normal levels but in which the nitrogen does not benefit the plant. The resulting symbiosis is characterized as nitrogen fixing but ineffective. The original mutation, which removes the N terminal end of the GlnD nitrogen sensor protein, was shown during this project to have significant effects on the bacterial nitrogen stress response. We have now shown that a standard model of GlnD action, in which GlnD initiates a signaling cascade by modifying the GlnB and GlnK proteins, is not adequate to explain the effects of the GlnD mutation. These results imply the existence of an alternate signaling pathway. We had also speculated that the bacteria might be converting the nitrogen into a compound that the plant could not metabolize. We now have evidence supporting this idea. The speculation included the possibility that this compound is part of a novel feedback mechanism that coordinates plant and bacterial metabolism during nitrogen fixation.

Unraveling the Regulation of Terpenoid Oil and Resin Biosynthesis for the Development of Biocrude Feedstocks

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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 (diesel and kerosene range) and bioproducts. This project is aimed at providing an improved understanding of oil and oleoresin biosynthesis. We are building on continuing advances using peppermint essential oil biosynthesis in glandular trichomes as a model system. In 2010 we published a cover page article in *Plant Physiol*, reporting on the development of a quantitative mathematical model describing the determinants of mint oil yield and composition under various environmental conditions. We are now extending these mathematical concepts to other essential oil producers.

The oil of Citrus peel, which contains primarily the combustible monoterpene limonene, is produced by a specialized cell type (epithelial gland cell or ECs) that is similar to that in peppermint glandular trichomes. During year one of the funding period, we measured the peel oil produced at different stages of Citrus. We also counted the number of oil-accumulating cavities and calculated, using stereological measurements, the amount of oil accumulated in cavities of different size, and extrapolated the total oil yield capacity of the peel. During year two, we continued these measurements with an independent set of fruit. These particular measurements and calculations have been completed and we achieved good convergence of oil yield extrapolations from microscopic data with actual oil yield measurements. This may sound trivial, but it actually involved the acquisition of tens of thousands of data points. The main reason for these tedious efforts was that, for the first time, we were able to correlate macroscopic measurements (oil yield determined by distillation) with the biosynthetic capabilities of ECs.

To further characterize oil biosynthesis in ECs, we developed a protocol for the isolation, using laser capture laser microdissection and pressure catapulting (LMPC), of ECs from resin-embedded Citrus peel tissue samples. We also developed a protocol for the isolation of RNA from these isolated ECs, converted the RNA to cRNA, which was then hybridized to Citrus microarrays. For comparisons we went through the same protocols with RNA isolated from mesophyll parenchyma cells (PCs) that are located next to ECs in the peel but likely do not have the same biosynthetic capabilities, particularly with regard to the synthesis of essential oils. Cells were harvested from fruit at two different developmental stages (28 and 41 mm equatorial diameter), with three biological replicate for each cell type (total of 12 microarray hybridizations). This was another very tedious effort as thousands of cells had to be collected for each individual sample. When we analyzed the microarray data obtained with these specialized cell types; however, the importance of having cell type-specific data became immediately apparent. Based on a principal component analysis (PCA) ECs had significantly different overall gene expression patterns when compared to PCs. Genes known to be involved or putatively related to essential oil biosynthesis were upregulated in EC versus PC comparisons. We are currently also evaluating the cell-type specificity of Citrus monoterpene biosynthesis with immuno-histochemical studies. We generated polyclonal antibodies against (+)-limonene synthase. Preliminary data indicate that this enzyme is expressed exclusively in leucoplasts of ECs. Enzyme assays with peel extracts are ongoing to help us link gene expression with oil measurement data. Taken together our data sets will then be used to feed a quantitative kinetic mathematical model, which will be used to test the accuracy of our knowledge about the regulation of the peel monoterpene pathway.

A third project area pertains to the development of a mathematical model of oleoresin formation in resin ducts of conifers (loblolly pine as a model system). This project required extensive methods development, in particular with regard to estimating the total volume of resin present in needles, twigs, shoots, branches and trunks. We have also worked hard on establishing the methods for obtaining RNA from the ECs lining the resin ducts. We have essentially completed the method development aspects of the project and are now in data acquisition mode. The current highlight is a 3D model of a small portion of a loblolly pine needle that focuses on visualizing resin duct volumes.

Biohydrogen Production by a Photosynthetic Bacterium

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Funding:	$170,000

Photosynthetic microbes can produce the clean-burning fuel hydrogen gas using one of nature's most plentiful resources, sunlight. The anoxygenic photosynthetic bacterium Rhodopseudomonas palustris, has a remarkable ability to obtain electrons for hydrogen generation from green plant-derived biomass and to efficiently absorb both high and low intensity light energy to form the ATP that is needed for this process. Microbes synthesize a wide variety of photosensory regulatory proteins in order to sense and respond to signals derived from light. One such family of photosensory regulatory proteins is known as bacteriophytochromes (BphPs). These are most often configured as light-regulated signal transduction histidine kinases which undergo photoconversion in order to transmit a light signal via a regulatory cascade that involves phosphotransfer. Despite an abundance of in vitro work characterizing photoconversion of BphPs, detailed molecular understanding of the physiological action of BphPs in photosynthetic organisms is lacking. Most of our current knowledge has been generated in R. palustris. Two BphPs in R. palustris, BphP2 (Rpa3015) and BphP3 (Rpa3016), have been studied extensively in vitro. In vivo studies have shown that they regulate expression of the pucBAd operon for light harvesting in response to low light intensity, but mechanistic information about how this happens is lacking. Regulation of pucBAd in R. palustris can be used as a model system to study BphPs and their regulatory cascades. Our aims for this project are to (1) determine how BphPs are able to function under anaerobic conditions since the known chromophore for these proteins, biliverdin, is synthesized only aerobically; (2) identify the other components of the regulatory cascade required for expression of pucBAd; and (3) determine the specific signal(s) sensed by the regulatory cascade that controls pucBAd expression, and determine which component(s) of the regulatory cascade sense these signal(s). By pursuing these aims, we will gain greater insight into how an important family of photosensory regulatory proteins integrates signals from light into physiological responses important for hydrogen gas production.

Hydrogenases of Methanococcus Maripaludis

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Funding: $300,000

The hydrogenotrophic methanogens play central roles in anaerobic decomposition, hydrogen metabolism, and methane production. Using the model hydrogenotrophic methanogen Methanococcus maripaludis, we are characterizing electron flow pathways as they relate to energy conservation. Hydrogenotrophic methanogens use hydrogen or formate to reduce carbon dioxide to methane in four reduction steps. Our work addresses a long-standing conundrum regarding how these organisms generate net chemiosmotic membrane potential to drive ATP production. They have no typical electron transport chain. Instead, they generate a sodium-motive force at a methyl transfer step. However, the membrane potential gained was thought to be depleted in the energy-requiring first step of the pathway. The last step of the pathway has the potential to yield energy but no energy-conserving mechanism could be discerned. We identified a protein complex that supports the notion that the solution lies in the phenomenon of electron bifurcation, wherein a flavin-containing enzyme splits electron flow into two directions, one energy-yielding and one energy-requiring, and couples the two. The protein complex contains the enzymes for the last and first steps of the pathway, providing the physical means to couple them. We are characterizing this protein complex biochemically in order to prove that electron bifurcation occurs. In addition, we are studying how the organism partitions electrons flowing from each of the alternate electron donors, hydrogen and formate, to the catabolic and anabolic reduced products, methane and biomass.

Protein Scaffolding for Small Molecule Catalysts

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Funding: $150,000

We are developing methods for designing peptides and small proteins to form scaffolding around small molecule catalysts. We have designed three peptides predicted to enhance the hydrogenase activity of catalysts developed by Dan Dubois, and Wendy Shaw at PNL is currently characterizing these experimentally. We are also designing peptide scaffolding around small molecules which we can test in the laboratory, and are starting to test these as well. The goal is to develop general methods for designing hybrid peptide/small molecule materials and catalysts and to validate these experimentally.

Dissection and Manipulation of LRR Domains in Plant Disease Resistance Gene Products

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Funding: $170,000

Leucine-rich repeat (LRR) protein domains offer a readily diversifiable platform - literally, an extended protein surface - for specific binding of very diverse ligands. The present project has addressed the following overlapping research questions:

- How do leucine-rich repeat proteins recognize their cognate ligands?
- What are the intra- and inter-molecular transitions that occur that cause transmembrane LRR proteins to switch between “off” and “on” states?
- How do plants use LRR receptor proteins to activate disease resistance?
- Can we synthetically evolve new LRR proteins that have acquired new ligand specificities?

In the past year we made substantial progress on these aims, with activity in five areas (five manuscripts).

(1) One clear and tangible contribution is the public release of a bioinformatics website that we developed, www.plantpath.wisc.edu/RCM, where researchers can enter primary amino acid sequences for two or more related leucine-rich repeat proteins. The analysis identifies the sites on the predicted surface of the LRR that have been most conserved across these proteins. These sites are typically the key functional sites on the protein, such as ligand binding sites. A peer-reviewed paper describing and validating the approach was also published (Helft et al. 2011 PLOS ONE).

(2) Laura Helft, the first author of that paper, also defended her Ph.D. thesis last month, and the final chapter of that thesis (now being reformatted for journal submission) describes her success at using RCM (see above) and other data to guide synthetic (investigator-driven) evolution of an LRR-based receptor protein (FLS2) so that this plant immune system receptor protein recognizes a pathogen ligand it formerly could not recognize. The recognition is not as strong as we would like (high doses of pathogen-derived ligand are required to elicit a host defense response), but it is clear that the protein has new ligand recognition capacity that was not formerly in place.

(3) Postdoctoral scientist Yangrong Cao has completed research for a new manuscript reporting discovery of a key autophosphorylation site on FLS2, the plant immune system receptor for bacterial flagellin.

(4) Dr. Cao also completed final experiments for a revised manuscript that we had submitted to *The Plant Cell* in Aug. 2011 and, after receiving provisionally favorable reviews but with a request for more experimental data that we have now obtained, will now be resubmitted to that journal. That manuscript reports on the nature of the FLS2 receptor complex and physical features of FLS2 protein that impact function.

(5) We also participated in and co-authored collaborative studies that were published this year, showing that FLS2 is needed for Arabidopsis responses to Ax21, a pathogen ligand distinct from flagellin (Danna et al. 2011 PNAS).

Molecular Dissection of the Arabidopsis Holo-26S Proteasome

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Funding:	$180,000

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, little is known about the structure of the RP and the functions of many of its principal subunits. It has also become clear in recent years 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, each with distinct compositions and unique functions/specificities.

The goal of this renewal proposal is to better define 26S proteasome function and diversity in plants by a more complete analysis of the particles from Arabidopsis thaliana. During the current funding period, we developed a novel affinity method to rapidly isolate the core 26S proteasome intact from Arabidopsis seedlings. Deep mass spectrometric (MS) analysis of the preparations identified all the central CP and RP subunits and detected a number of post-translational modifications to individual subunits, including proteolytic processing, N and internal acetylation, and ubiquitylation, especially of RPN1 and RPN2 of the RP base. We also identified a number of accessory proteins bound substoichiometrically to the protease complex. Included are chaperones involved in proteasome assembly and maturation, the PA200(Blm10) protein that also caps the CP to form a unique PA200/CP proteolytic complex, the 4-membered family of RAD23 proteins that help shuttle ubiquitylated substrates to the proteasome, and a number of functionally unknown proteins that could alter the activity and/or specificity of the Arabidopsis 26S proteasome.

To help determine the functions of individual RP subunits, we have begun a reverse genetic analysis of the corresponding genes. Recent studies on the two genes encoding the RPT2 subunit of the RP base, revealed that this subunit has an important role in 26S proteasome assembly and is essential for proper sporophyte and gametophyte development, possibly through its role in regulating histone levels and thus nucleosome dynamics. Important to these varied processes are both the ATP-binding/hydrolysis and HbYX docking domains within the RPT2 protein. Whereas inactivation of RPT2b is without phenotypic consequences, inactivation of the RPT2a gene strongly compromises Arabidopsis growth and development and proteasome assembly. However, the suite of rpt2a phenotypes can be rescued by introducing transgenes expressing either RPT2a or RPT2b, indicating that the two isoforms are functionally redundant and that expression differences between the two loci are mainly responsible for the phenotypic differences. More recently, we have begun a reverse genetic analysis of the RPT4a and RPT4b pair. As above, both mutation and complementation studies revealed that the two RPT4 isoforms appear to be functionally redundant. Surprisingly insufficient levels of RPT4 generate an insensitivity to the hormone ABA in contrast to mutants in other proteasome subunits which generate ABA hypersensitivity, thus implying that individual subunits have substrate-specific functions. Once completed, our structure/function studies should help reveal how the population of 26S proteasome in particular, and protein turnover, in general, are used by plants to regulate their growth, development, and responses to their environment. By exploiting this knowledge, we hope to develop methods to manipulate proteasome function for the benefit of agricultural yield and the production of renewable biofuels.

Fluctuation X-Ray Diffraction of Membrane Proteins in Solution

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Funding:	$90,000

Work is in progress on two main projects:

(1) Development of a theory and algorithm for recovering the change in the structure of an uncrystallized protein on photoexcitation by means an ultrashort pump-probe experiment on individual protein molecules injected into the path of an x-ray beam from a free-electron laser. The protein will be photoexcited by a laser a very short time before being illuminated by the probe x-ray beam. The problem is more complicated than the corresponding time-resolved crystallography experiment since the orientation of the molecule whose diffraction pattern is being measured is unknown. However, we believe this problem is solvable by means of a kind of perturbation theory if the unexcited (or "dark") structure is assumed known. We have developed the theory of the algorithm, and work is now in progress on implementing the algorithm on a computer. If this works, it would greatly expand the scope of time-resolved structure determination of biomolecules since such molecular changes can be studied not in a crystalline environment but on individual molecules in solution and thus in environments much closer to those in which they are found in nature. A possible implication of this work is a greater understanding of fast changes in photosensitive molecules in processes like photosynthesis.

(2) The other major project in which we are currently engaged is also aimed at extracting structural information about biological particles from radiation from an x-ray free-electron laser (XFEL), such as now operating at Stanford in California. This is a machine built at a cost of hundreds of millions of dollars and produced x-rays of unprecedented brilliance. It is believed to offer a path to structure determination of biomolecules or viruses without the problematic requirement of crystallization. Nevertheless, the 3D structure of the particles needs to be determined from multiple 2D diffraction patterns of random unknown particle orientations, a circumstance which requires brand new theory. We have developed such a theory which shows great promise in simulations, and are currently working on applying it to experimental XFEL data from viruses that is now beginning to be deposited on public web sites, such as cxidb.org.

Engineering Selenoproteins for Enhanced Hydrogen Production

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Funding: $165,000

Hydrogenases are crucial enzymes in the production and utilization of hydrogen, which is an important potential source of clean energy. Archaeal enzymes of the [NiFeSe] group of hydrogenases have selenium at their active center, in the form of selenocysteine (Sec). Sec is found in many redox enzymes, where it provides catalytic power not matched by the related amino acid cysteine. Since Sec is incorporated into proteins with an elaborate re-coding machinery, it is not feasible to site directly incorporate Sec into designed enzymes. By engineering the enzymes and tRNA involved in genetically encoding Sec, we shall developed an Escherichia coli strain that is able to incorporate Sec in response to a any UGA codon without the need for the Sec re-coding RNA element and elongation factor. This strain will allow us to use the Sec encoding system to produce custom selenoproteins that will allow elucidation of the catalytic properties of Sec in the [NiFeSe] hydrogenase and in hydrogenase variants that will be assayed for enhanced hydrogen production.

DOE National Laboratories

Separations and Analyses (Mass Spectrometric Imaging of Plant Metabolites)

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Funding: $195,000

Plants integrate biochemical machineries that are distributed among different cell-types and subcellular compartments to achieve net metabolic conversions. Techniques that can track intermediate metabolites as they move through a distributed metabolic network, and simultaneously become chemically interconverted are needed to directly demonstrate the nature of the network and its regulation. Our long-term objective is to develop mass spectrometric imaging techniques and determine the distribution of plant metabolites at the level of a single cell and subcellular compartments; mass spectrometry not only allows positive identification of the many plant metabolites but can also reveal the substrates and precursors involved in each metabolic pathway. These techniques are being developed in the context of understanding plant metabolic processes that are integral to highly efficient energy capture and storage, and are therefore at the core of DOE's mission.

Analogous to matrix-assisted laser desorption ionization (MALDI), we are developing methods that use a laser beam to interrogate, sequentially, micrometer areas of a plant by vaporizing the surface contents of the tissue into a mass spectrometer. Rastering of the laser beam over the tissue produces a laterally-resolved image of the various substances within different structures of the plant. Repeated vaporization at the same focused point of a plant structure will produce a depth profile of the components. Our research also includes generating ions directly from the plant tissue by designing novel additives as pseudo-matrixes. By minimizing sample preparation, compositional integrity and spatial resolution of the analysis will be guaranteed. Identification of the metabolites is aided by new strategies in ion formation, fragmentation, and high-resolution mass analysis. Spatial resolution will be pushed to the low micron regime by optimizing the optics and by increasing the detection efficiency.

Dissecting Macromolecular Regulation and Organization of Lignin Biosynthesis

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Funding:	$250,000

Lignin is the most abundant terrestrial biopolymer after cellulose. The presence of lignin in cell wall biomass, however, renders a formidable obstacle impeding the efficient utilization of sugars in cell wall fibers for liquid biofuel production. Plant lignification is a tightly regulated developmental process. Lignin biosynthesis and deposition in the cell walls are also greatly influenced by environmental stresses. However, the molecular mechanisms underlying the regulation of lignin biosynthesis and deposition are not fully elucidated. In particular, we barely understand the regulatory mechanisms for its biosynthesis beyond the transcriptional level, for instance whether and how the biosynthetic pathways are organized subcellularly, whether the synthesis receives posttranslational regulation, executed by protein-protein interaction and macromolecular organization, and how the biosynthesis of lignin coordinates with other biological processes. To dissect the potential protein-protein interactions/enzyme organization in lignin biosynthesis, we are undertaking a research program with the multifaceted strategies of biochemistry, biophysics, cell biology, and molecular genetics. The long-term goals of our research are to understand the molecular mechanisms of regulation of plant lignification, and its coordination with other biological processes at posttranslational and subcellular levels.

PROGRESS IN FY2011

Based on yeast two-hybrid screening, we revealed that lignin biosynthetic enzymes, such as CCoAOMT, HCT, and COMT, potentially interacted with a set of catalytic- or non catalytic-structural proteins in vitro. Some of the interactions were further evaluated with the pair-wise yeast two-hybrid, pull down, and split luciferase assays. The subcellular localization/co-localization of a few prey proteins with lignin biosynthetic enzymes were monitored. To explore biological functions of the specific interaction events and of the involved prey proteins, we examined a set of T-DNA insertion mutant lines deficient in the genes encoding prey proteins. The effects of their deficiencies on phenylpropanoid-lignin biosynthesis were preliminarily evaluated. Further, the selected prey proteins were used as the baits to search their potential interaction patterns in yeast two-hybrid screening. We expect to dissect the molecular basis and biological roles of those interactions in either signal transduction or metabolic organization/metabolic channeling for regulating phenylpropanoid-lignin biosynthesis. Furthermore, we will explore more broadly the potential interactions afforded by all the lignin biosynthetic enzymes.

Our studies will lead to a detailed understanding of the regulatory mechanisms underlying plant lignification and the coordination of lignin biosynthesis with other biological processes. This knowledge will underpin the innovative strategies for manipulating lignin biosynthesis to improve the efficiency of biofuel production, and thus, contribute to our national energy security.

Energetics and Structure of the ZIP Metal Transporter

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Funding:	$450,000

Electron transfer reactions in photosynthesis require multiple metal centers for redox-catalyses. Metal uptake from the soil to the chloroplast sink involves multiple transport steps across a series of membrane barriers. The long-term goal of our research is to understand the chemical principles governing selective binding and energized movements of metal ions in metal transporters. We will use direct biophysical measurements and x-ray crystallography to study the ZIP (ZRT, IRT-like Protein) metal transporters. Specifically, we will (1) identify a ZIP model protein that can be purified in a sufficient quantity for biophysical and structural analyses, (2) determine the energetic mechanism for ZIPs, and (3) crystallize a prototypic ZIP for x-ray analysis. The proposed studies may reveal how metal coordination chemistry is exploited to move metal ions across the membrane barriers to reach their final destinations in the photosynthetic complexes. This project supports DOE's mission to understand and to adapt strategies used by plants and microorganisms to capture, store, and mobilize energy.

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

Lignin is an aromatic natural polymer derived from the oxidative polymerization of different hydroxycinnamyl alcohol monomers, the monolignols. The presence of lignin in plant cell wall imparts the structural integrity; however, it negatively affects the utilization of cell wall fibers in agricultural and industrial applications, in particular, the use for biofuel production. Although lignin biosynthesis has been studied for decades and considerable efforts were dedicated to modulating lignin content in order to utilize cell wall fibers more economically, novel biotechnology/methodology is still required for efficiently manipulating plant lignification.

Polymerization of lignin starts with the oxidative dehydrogenation of monolignols, followed by cross-coupling of the resulting phenoxy radicals. The para-hydroxyls (i.e., 4-OH) of monolignols are implicated to be critically important for radical generation, and subsequent coupling. Therefore, we rationalized that a chemical modification, for example the methylation of the phenol, would prevent radical generation and deny the derived monolignols any participation in the subsequent coupling process, thus reducing the quantity of lignin produced.

PROGRESS IN FY2011

Using the strategy of structure-based iterative saturation mutagenesis, we created a set of phenolic O-methyltransferase variants that entailed the ability for para-methylation of monolignols, termed monolignol 4-O-methyltransferases. Subsequent crystal structure determination of the mutant variant in complex with monolignol and co-substrate revealed the molecular basis for its broadened substrate preferences and the regiospecific para-methylation. With the engineered enzyme, we showed that genetically perturbing the hydroxycinnamyl alcohol structure by etherifying the phenol indeed prevents the monomer from participating in lignin polymerization. Expressing the created enzyme in Arabidopsis substantially reduced lignin content of the cell wall, and lowered the release of the lignin-diagnostic monomers from reactions cleaving ß-aryl ether linkages. Concomitantly, the transgenic plants accumulated de novo synthesized 4-O-methylated soluble phenolics and “wall-bound” esters. The lower lignin levels of transgenic plants resulted in higher saccharification yields. Assessment of the functions of the created enzymes in modulating phenylpropanoid-lignin biosynthesis in bioenergy crops is undertaken.

Together the information from this study offers scientific underpinnings and a novel strategy for manipulating lignin biosynthesis to improve the efficiency of biofuel production and thus contribute to decreasing our dependence on petrochemical fuels. The project will contribute to DOE’s mission in energy security.

Modification of Plant Lipids

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Funding:	$1,000,000

This work addresses the BES mission with respect to gaining foundational knowledge regarding the conversion of renewable resources into fuels, chemicals and other energy-enriched products. The project focuses on the production of plant oils, which are the most abundant energy dense form of stored carbon in plants. Specifically, we are studying the molecular basis for chiral lipid-modification reactions using fatty acid desaturation as a model. We employ x-ray crystallography, spectroscopy, molecular genetics and biochemistry to probe structure-function relationships within these enzymes. Understanding the factors that control the selectivity and specificity of these processes is allowing us to redesign lipid-modification enzymes with improved function. Our ultimate goal is to provide the knowledge base for the metabolic engineering of improved plant lipid accumulating non-food crops.

PROGRESS IN FY 2011

Major advances in our understanding the molecular basis for regioselectivity in the acyl-acyl carrier protein (ACP) desaturase enzymes were made. We demonstrated that regioselectivity is governed by a remote control mechanism at a distance of 27A from the site of double bond insertion. Using this mechanistic knowledge we were able to introduce two mutations into the D9 desaturase converting it into a D4 desaturase. In future work, we hope to be able to use this knowledge to engineer enzymes with new regioselectivities for the production of novel renewable industrial feedstocks in plants.

In related work, a laboratory-evolved 16:0-D9 desaturase enzyme was expressed in Arabidopsis and, in conjunction with pathway engineering, we created a plant that accumulates 72% of w-7 fatty acids, the precursor for industrial production of 1-octene, a feedstock for which the annual demand exceeds 500,000 tons. Progress was also made on understanding the oligomeric structure of plant desaturase enzymes. We discovered that integral-membrane desaturase enzymes, like their soluble counterparts, and the yeast OLE1, form dimers in vivo. Interestingly, desaturases form both homodimers and heterodimers with desaturases that have distinct regioselectivities. This latter observation is interesting in that heterodimeric enzymes consisting of FAD2 and FAD3 enzymes, for example, may constitute a metabolic channel in which the substrate for FAD2, oleic acid could be desaturated to produce linoleic acid which in turn would be further desaturated by the FAD3 enzyme to produce linolenic acid. Experiments to test this hypothesis are currently underway.

Quantitative analysis of Central Metabolism and Seed Biomass Synthesis in Brassica napus

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Funding:	$500,000

Plant biomass is of increasing importance as renewable resources for the production of biofuels and of feedstocks for the chemical industry in order to replace petroleum based materials. As a basis for rational engineering of seeds and other plant storage organs, the goal of the Schwender group is to increase the basic understanding of the functioning of storage metabolism in plants – from a perspective of biochemical reaction networks. Of central interest here is the process of allocation of carbon and nitrogen resources provided by the mother plant to different storage products (oil, protein and starch) in a carbon sink organ like a developing seed. Cultures of developing embryos of Brassica napus (rapeseed) and other brassicaceae turned out to be excellent in vitro models to study development and storage synthesis in an oil seed. Empirical findings resulting from embryo cultures are used to develop, validate and apply mathematical models and computer simulation. Our special focus and expertise is in methods of stable isotope (carbon-13) metabolic flux analysis, flux balance analysis, and enzyme kinetic modeling. The combination of experimental and computational tools helps to quantitatively describe and obtain a deeper understanding of plant metabolism. It also provides predictive tools as a basis of rational engineering of carbon and energy storage in plants.

PROGRESS IN FY 2011

We refined and published a large scale metabolic model of a developing seed of Brassica napus. Based on embryo cultures, metabolic flux analysis studies were performed, characterizing about 10 genotypes of Brassica napus that differ in oil content.

We furthermore worked on applying our experimental and modeling methodology to a different oil seed species from the Brassicaceae family which is much easier to be genetically transformed than Brassica napus. A number of genetic constructs were started which should allow us to test the effect of transgenic alterations with regards to carbon partitioning and storage synthesis. To extend our analytical capabilities in (carbon-13) metabolic flux analysis, we worked out analysis protocols with a newly purchased gas chromatograph MS/MS instrument.

At BNL the Schwender group interacts with colleague A. Rogers who has developed a unique BNL facility, i.e., an automated platform for simultaneously assaying an array of metabolic enzymes. Other collaborations within BNL are with the Shanklin group and Xu group regarding storage oil synthesis in various plant species and algae. Further international collaborations exist with academic and industrial partners.

The project strongly aligns with the goals of the Basic Energy Sciences/Physical Biosciences program. Specifically our research aims for “a fundamental understanding of the complex processes that convert and store energy in living systems.” For this purpose our research combines “both experimental and computational tools.”

Engineering Active Biological Material Interfaces with Nanotechnology

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Funding:	$986,000

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.

Biological Principles of Energy Transduction: Basis for the Designed Synthesis of Hydrogen Catalysts

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Funding: $500,000

We propose to obtain a molecular understanding of how the base metals in biological enzymes act to effectively stabilize H^+ and H- ions associated with H_2 synthesis/degradation and efficiently couple the transfer and storage of substrates (i.e., electrons and protons/hydrogen). These goals will be accomplished by (1) determining how changes in active site coordination affect rates of catalysis in isolated hydrogenases, (2) understanding how structural changes involving active site ligands couple to the surrounding protein matrix to alter substrate barriers that enhance rates of catalysis, and (3) identifying oxygen binding mechanisms and the role of oxidative modifications in affecting long-term enzyme function. It is expected that enhanced rates of enzyme catalysis will be achieved by reengineering the second coordination sphere around the active site to control the ligand environment and through the modification of protein stability to diminish diffusional barriers associated with substrate movements through the protein matrix.

Specifically in FY 2010 the [Ni-Fe] hydrogenase has been expressed using a homologous system, purified and used to (1) collect infrared and Raman spectral data that establish both the structural integrity of the system and (2) provide constraints for computational measurements that simulate the active site structure and relationships to surrounding protein elements that control reactivity. In collaboration with Professor Judy Wall at the University of Missouri Columbia, expression of the hydrogenase enzyme is being optimized to provide the needed amounts of mutant enzymes for detailed kinetic measurements. Initial computational predictions suggest a novel coupling between the active site structure and the protein environment around the diatomic ligands that can be tested using site-directed mutagenesis in concert with the available crystal structures. Complementary measurements that explore the active site environment involved the synthesis and structural characterization of approximately 10 different biomimetics of the active site involving the inclusion of different peptide elements that modify the polarity and proximity of nitrogen ligands that act as hydrogen acceptors. Initial electrochemical measurements indicate that inclusion of small amino acid side chains (i.e., glycine) at the interface between the active site and the peptide linker enhanced hydrogen splitting activity – providing a means to test structure/function correlations regarding how optimization of the first shell coordination sites enhance catalytic rates.

Separations and Analysis

Institutions Receiving Grants

Energetics of Nanomaterials

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Funding:	$165,000

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 bringing expertise in nanoparticle synthesis and low temperature heat capacity measurements, Alexandra Navrotsky at University of California Davis bringing unique capabilities in high temperature calorimetry and the measurement of enthalpies of formation and surface energies, and Nancy Ross at Virginia Tech engaging in neutron scattering studies. Together this group seeks understanding of the systematics of surface energies and the hydration of nanoparticle surfaces and their effects on stability and reactivity. Current work has shown that different structures have systematically different surface energies, leading to crossover in thermodynamic stability of polymorphs at the nanoscale, and to substantial changes in the position of phase boundaries for dehydration and oxidation-reduction reactions. 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.

Ion Production and Transport in Atmospheric Pressure Ion Source Mass Spectrometers

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Funding:	$140,000

During the past year, we have made progress in three broad areas of our project. In the first area, our experimental work with inductively coupled plasma mass spectrometers, we have focused on changes in instrument sensitivity caused by changes in sample composition, or in the jargon of analytical chemists, “matrix effects.” We have tested a recently-published hypothesis that large concentrations of matrix species deplete populations of excited argon atoms, which are thought by some in the community to be key reactants for the production of analyte ions. Using laser pump and probe methods, we measured spatially resolved densities of argon metastable atoms, both in the presence and absence of ten representative matrix species. Contrary to the predictions of the published model, the addition of a high concentration of matrix species increased rather than reduced the densities of key excited levels of neutral argon. Our time-resolved measurements suggest a different model for matrix effects, in which the addition of a matrix leads to radiative cooling of electrons in the plasma.

Matrix effects are also thought to arise in the second vacuum stages of ICP mass spectrometers, where analyte ions are shaped into a beam that is delivered to the instruments' mass analyzers. To study this possibility, we have taken advantage of the unique geometry of an ICP-MS manufactured by Bruker, in which the ion beam undergoes a right-angle bend between the skimmer cone and the mass analyzer. The open ring lens that is used to bend the beam allows us to use planar laser-induced fluorescence to image a cross section of the beam in front of the entrance to the mass analyzer. The effect of matrix on the radial distribution of analyte ions within the beam is dramatic. The addition of 1.5 mM lead to a calcium solution caused the calcium signal to drop by an order of magnitude. The experiments demonstrated that the loss of signal was not due to a loss of beam intensity, but rather to a shift in the beam position so that a large fraction of the beam missed the entrance to the mass analyzer.

The second general area of research is the development of models of flow through the vacuum interface if an ICP-MS, based primarily on Direct Simulation Monte Carlo (DSMC) codes. This year we have used the simulation to study the spread of the analyte beam in the first vacuum stage in an effort to understand experimental differences between the behaviors of Ca and Ba test analytes. We have also used the simulation to understand experimentally recorded differences in the performance of a variety of skimmer cone designs. Finally, a student has developed a DSMC code for electrons that will be useful in interpreting our experimental studies of matrix effects.

The third general area is the fundamental characterization of ambient ionization sources for mass spectrometry. We have focused most of our effort this year on helium plasmas that are used as ionization sources. In particular, we have generated time- and space- resolved maps of key reactive species in a dielectric barrier discharge using a combination of emission and fluorescence imaging. Time-dependent maps of the densities of helium metastable atoms, highly-excited helium atoms, ground-state nitrogen molecular ions, excited nitrogen molecular ions, and excited nitrogen neutral molecules reveal the interactions among the flowing helium gas, the ambient atmosphere, and exciting voltage during one cycle of the exciting waveform. Our results support the idea that, in a pure helium discharge extending into the atmosphere, Penning ionization of nitrogen by helium metastables a key step in the production of analyte ions. However, the addition of a small amount of hydrogen to the plasma gas changes the picture completely, quenching the helium metastable atom population, while at the same time increasing the production of analyte ions. In ongoing experiments we are changing the hydrogen composition of the plasma gas in an effort to find the optimum composition for practical application of the plasma as an ambient ionization source.

Photoacoustic and Thermal Effects in Particulate Suspensions

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Funding:	$135,000

The direction of intense ultrasound at a liquid-gas interface results in the formation of an ultrasonic fountain and generates both mist and vapor from the liquid. Investigation of a published report describing ultrasonic distillation of water-ethanol mixtures that yields complete separation of ethanol from water has been carried out. Note that such a process would be a highly important development in making ethanol from biomass, as distillation is an energy intensive process. In the experiments carried out here the composition of the vapor and aerosol above an ultrasonic fountain was determined as a function of irradiation time and compared with the results of sparging, which refers to bubbling dry gas through a mixture. Experimental data were obtained using gas chromatography, refractive index measurement, nuclear magnetic resonance, and spectrophotometry. Experiments were carried out with ethanol-water and ethyl acetate-ethanol solutions, cobalt chloride in water, colloidal silica, and colloidal gold. The experiments show that ultrasonic distillation produces separations that are less complete than what is obtained using sparging and directly contradict several papers published on ultrasonic distillation. The work here shows that ultrasonic distillation does not give perfect separation of ethanol from water-ethanol mixtures.

The Ludwig-Soret effect, sometimes referred to as thermal diffusion, describes the separation of mixtures in the presence of a temperature gradient. We have introduced a new experimental method for measuring parameters for the Ludwig-Soret effect based on recording the entire distribution of the components in space. The interpretation of the data is based on our solution to a nonlinear equation in the limit of long time. We have introduced an experimental method based on the use of a scanning confocal microscope to monitor concentrations in the direction of the thermal gradient. Experiments where the spatial distribution of fluorescence from fluorescein labeled nanoparticles in water were carried out showing the capability of the method for determining a parameter known as the thermal diffusion factor. The theoretical work done here on thermal diffusion gives, for the first time, an exact solution for the nonlinear differential equation describing the Ludwig-Soret effect for a binary mixture in a constant temperature gradient. The same differential equation of motion is solved in the limit where mass diffusion is neglected, showing that shocks are generated. We also show that for a temperature field of infinite extent, distributions originally localized in space move at long times with constant speed with self similar form.

Theoretical work has been carried out to determine the character of photoacoustic waves in a one-dimensional solid or fluid with a sound speed that varies sinusoidally in space. Closed form solutions for the acoustic pressure and all properties of the photoacoustic waves are found. The analysis is based on the wave equation for pressure for the photoacoustic effect, which reduces to an inhomogeneous Mathieu equation, the solutions to which have received virtually no treatment in the literature. We give a general solution for arbitrary excitation of a periodic structure based on the use of new eigenfunction and orthogonality relations for the integer order Mathieu functions. We show that the solutions possess the space equivalent of subharmonic frequency generation, a property not previously investigated in phononic structures. The work shows that the photoacoustic effect can be generated as easily within band gaps as outside of them. As well, a solution for the photoacoustic pressure for a source confined in space based on new traveling wave Mathieu functions has been found. Results of the calculations show a new confinement of photoacoustic waves in space when the waves are generated within band gaps, and an amplitude enhancement of the wave amplitudes at the edges of the gaps irrespective of whether the excitation is within or outside the gaps.

Energetics of Nanomaterials

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Funding:	$110,000

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 bringing expertise in nanoparticle synthesis and low temperature heat capacity measurements, Alexandra Navrotsky at University of California Davis bringing unique capabilities in high temperature calorimetry and the measurement of enthalpies of formation and surface energies, and Nancy Ross at Virginia Tech engaging in neutron scattering studies. Together this group seeks understanding of the systematics of surface energies and the hydration of nanoparticle surfaces and their effects on stability and reactivity. Current work has shown that different structures have systematically different surface energies, leading to crossover in thermodynamic stability of polymorphs at the nanoscale, and to substantial changes in the position of phase boundaries for dehydration and oxidation-reduction reactions. 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.

Metal-Organic and Zeolite Imidazolate Frameworks (MOFs and ZIFs) for Highly Selective Separations

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Funding:	$148,000

Metal-organic and zeolite imidazolate frameworks (MOFs and ZIFs) are investigated for the realization as separation media with high selectivity. These structures are held together with strong bonds, making them architecturally, chemically, and thermally stable. Therefore, employing well designed building units, it is possible to discover promising materials for gas and vapor separation. In this project, we are undertaking efforts (1) to examine the use of MOFs with well-defined open metal sites for binding of gases and small organic materials, (2) to develop a strategy for producing MOFs and ZIFs that combine high surface area with active metal sites for their use in gas adsorption and separation of small organic compounds, and (3) to increase the chemical and thermal stability of MOFs and ZIFs for the gas separation under humid conditions.

Computer Simulation of Proton Transport in Fuel Cell Membranes

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Funding:	$160,000

This project involves a unique multiscale computer simulation methodology for studying proton solvation and transport in proton exchange membranes (PEMs) for fuel cell applications. A key component of the project is a novel atomistic molecular dynamics (MD) simulation approach called the Self-Consistent 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. This study includes the critical Grotthuss shuttling process (hopping transport) and vehicular transport (classical Einstein diffusion) on the same footing. Several significant advances of the SCI-MS-EVB approach have been developed and will be extended in the future, including a force-matching method to derive accurate SCI-MS-EVB model parameters from ab initio molecular dynamics (AIMD) simulations. Algorithmic advances and enhanced code scalability are proposed that will further allow the SCI-MS-EVB simulations to access increasingly large system sizes and long simulation times. Key results obtained during the past funding period have revealed the remarkably complex behavior of the proton solvation and transport in the hydrophilic domains of NafionTM, including an unusual and unexpected anti-correlation between vehicular transport and hopping transport that increases with decreasing PEM hydration levels. Results have been further obtained on the water dynamics in NafionTM as well as large-scale MD studies of various proposed NafionTM morphological models. Novel mesoscopic-scale simulations of proton transport in PEMs have also been developed, with key extension proposed, which include a multiscale bridging of the atomistic SCI-MS-EVB data to mesoscopic proton transport modeling, coupled to complex PEM morphology. Future applications of the overall multiscale simulation approach are described for PEMs such as NafionTM, as well as for other promising PEMs. Important collaborations with experimental researchers at Stanford University and Colorado School of Mines are highlighted.

Selective Recognition of Heavy Elements by Protein-Based Reagents

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Funding:	$165,000

OVERALL RESEARCH GOALS

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.

SIGNIFICANT ACHIEVEMENTS IN 2011

(1) Uranyl-selective 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 have been shown to bind uranyl at nM affinities. We performed further rational protein engineering on one of the uranyl-binding protein. We were able to improve the uranyl-binding affinity to 0.2 fM with a 1,000-10,000-fold selectivity over any other metal ions tested. To our knowledge, this is the first system to be able to directly enrich uranyl from sea water. Our results show a major breakthrough in the ability to selectively enrich the uranyl cation over other ions.

(2) Unnatural peptides to selectively bind trivalent actinide ions. We have synthesized a series of modified lanthanide/actinide-binding peptides. Some of these reagents can selectively bind trivalent actinides over trivalent lanthanides by means of introducing soft-donor atoms into a peptide known as a lanthanide-binding tag (LBT). Fluorescence spectroscopy has been used to measure the dissociation constant of each metal-peptide complex. A 10-fold selectivity was obtained for Am^{3+} over the similarly-sized lanthanide cation, Nd^{3+}, when the asparagine on the 5th position of LBT was mutated to a cysteine and further functionalized by a pyridine moiety.

Fluoropolymers, Electrolytes, Composites and Electrodes

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Funding:	$250,000

The overall objective of this research project is to provide new electrolyte membranes and electrode materials consisting of integrated catalysts and fluorinated electrolytes for use in PEMFC power sources. In FY 2011 work toward these objectives was pursued in four topical areas: (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. In topic 1, fluoro-ionomers having equivalent weights between 600 and 900 g/equiv were prepared and processed into membranes. The materials are co-polymers of tetrafluoroethylene with trifluorovinyl ether (TFVE) co-monomers having fluorosulfonimide protogenic groups. Some polymers were partially crosslinked using difunctional TFVE units during the polymerization, and others consisted of blends of low and high EW ionomers. Ionic conductivities are generally improved relative to Nafion PFSA ionomers, with the best conductivities generally corresponding to the lowest EW ionomers. In topic 2, oligomeric PFCB ionomers having a high degree of sulfonation and end groups consisting of phenylphosphonic acid (PPA) groups were prepared. One intended application for these ionomers involves attachment onto catalyst support surfaces via the PPA end groups, to allow for a robust integration of very low EW ionomers into electrodes, when such ionomers would otherwise wash out of the electrode with product water. In topic 3, a wide range of mesoporous carbon catalyst supports was prepared using resorcinol/formaldehyde chemistry for making RF sols (which produce carbon upon high-temperature pyrolysis) containing silica sols as templating agents, and also zirconia nanoparticles as anchoring agents for PPA-based ionomer electrolytes. Extensive characterization of support materials was accomplished using electron microscopy/EDX, nitrogen porosimetry, and X-ray diffraction. Platinum deposition was demonstrated for all supports, and electrolyte immobilization was demonstrated for supports containing integrated zirconia, using electrolytes having PPA groups. This work had identified a new strategy for integrating electronic and ionic conduction within catalyst supports in PEMFC power sources. Finally, in topic 4, an electrospinning approach to making nonwoven fibrous mats of PFCB-based polymers was demonstrated. This work could hold promise for controlling water transport within PEMFC membrane-electrode assemblies.

Imaging of Conformational Changes

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Funding:	$210,000

Our ultimate objective is to develop methods for the detection and control of rotary conformational changes for single molecules in real time. In the initial funding period differential barrier height imaging (DBHI) and tip-enhanced resonance Raman spectroscopy (TERS) have been combined in a new instrument with the potential to make correlated maps of Raman band intensities and polarizations for molecules undergoing or having undergone electric-field induced conformational change. Tailor-made molecular rotors needed for the investigation have been prepared by standard methods of covalent synthesis; 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 represent a significant contribution to the 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:	$220,000

In this project, real-time imaging methods are being developed that use individual reactant/adsorbate molecules as probes of surface chemical functionality and reactivity. Our approach is based on observations of individual molecules using total internal reflection fluorescence microscopy (TIRFM), including high-resolution methods involving resonant energy transfer and quenching. Specific aims include the development of multicolor TIRFM methods that permit simultaneous identification and spatial mapping of multiple surface functional groups, methods that provide quantitative information about the kinetics and energetics of reactants at catalytic interfaces, and single-molecule TIRFM methods that employ resonance energy transfer (FRET) to probe the local molecular environment, and to identify and measure reaction rates at individual immobilized catalytic sites. Methods like those proposed here will be necessary for the development and characterization – and especially the mechanistic understanding – of advanced catalysts that modify the environment of the active site (using non-covalent interactions) to improve reactivity, selectivity, and longevity. Such catalysts will be particularly important for reactions in complex liquid and multiphase media and for biomass-derived feedstocks that contain large and multifunctional (e.g., amphiphilic) reactant molecules.

Ion Formation and Fragmentation in UV and IR Soft Laser Desorption Ionization

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Funding:	$145,000

There are currently three studies underway in this project. Their objectives and latest results are summarized below.

SINGLE CELL ANALYSIS OF MICROORGANISMS ON SILICON NANOPOST ARRAYS (NAPA) BY LASER DESORPTION IONIZATION MASS SPECTROMETRY

Understanding metabolic processes in microorganisms, such as Saccharomyces cerevisiae, can reveal how these systems grow, develop and interact with the environment. Whereas high-throughput microarray and proteomics techniques help to explore the link between the genome and particular phenotypes, there is no such platform available for metabolic analysis. Consensus metabolic networks have been developed for yeast but their large scale testing also requires close to global analysis of metabolites. Silicon nanopost arrays (NAPA) are a novel matrix-free platform for the direct analysis of metabolites in cells by laser desorption ionization mass spectrometry (LDI-MS). NAPA requires minimal sample preparation, has ultralow limits of detection (~300 zeptomoles) and can be used for the analysis of small cell populations and single cells of yeast.

Yeast analysis on NAPA with LDI-MS produced signal for over one hundred metabolites (19% of the known S. cerevisiae metabolome) in very small cell populations, i.e., less than 100 cells. Direct single cell analysis was also achieved with 4% of the known metabolites detected. The identified metabolites belonged to 63 of the 94 major metabolic pathways with the majority of them involved in the biosynthesis and degradation of amino acids, carbohydrates, nucleotides, and lipids. Quantitation capabilities were also demonstrated by comparing the ion yields of common amino acids for populations ranging from a single cell to ~80 cells. Furthermore, metabolic state changes were observed for cell populations exposed to oxidative stress. Directly probing diverse metabolic changes in microorganisms, such as Saccharomyces cerevisiae, enables the large-scale exploration of the functioning genome. Understanding these processes also reveals how heterogeneous microbial populations evolve and interact with their environment.

SUBCELLULAR ANALYSIS BY LASER ABLATION ELECTROSPRAY IONIZATION (LAESI) MASS SPECTROMETRY

Subcellular variations in metabolite concentrations result from the presence of organelles and active transport inside the cell. Although certain metabolite distributions can be followed by fluorescence microscopy or SIMS, most subcellular work relies on fractionation based on cell disruption and differential centrifugation to separate the organelles by their density. While this process preserves the distribution of large molecules, e.g., proteins, metabolite concentration gradients are disrupted. In the last reporting period, laser ablation electrospray ionization (LAESI) mass spectrometry was utilized to explore the metabolic makeup of single cells at atmospheric pressure. Here we demonstrate in-situ subcellular metabolic analysis using microdissection with LAESI mass spectrometry.

The membrane of a single tissue embedded epidermal cell was cut along the inner edge of the cell wall and peeled back with the microdissection needle to expose the cytoplasm. In transmission illumination, the cell nuclei became visible without histological staining. As the sharpened tip of the optical fiber was comparable in size to the ~20 µm cell nucleus selective ablation of the nuclear region was possible. Over 30 metabolites were detected from a single nucleus and more than half of them were tentatively assigned to primary metabolites including amino acids and carbohydrates. To gain insight into intracellular metabolic heterogeneity, the exposed cytoplasm, away from the nucleus, was also ablated and analyzed. Large differences were observed in the abundance of some metabolites, such as alliin and thymine, between the cell nucleus and the cytoplasm. The presented subcellular analysis method has the potential to provide a better understanding of the organization and function of metabolites within regions inside a cell. Further studies will focus on examining the subcellular transport of metabolites.

CELL-BY-CELL IMAGING AND BIOMARKER DISCOVERY BY LAESI MASS SPECTROMETRY

LAESI mass spectrometry has been successful at detecting numerous metabolites from tissues and single cells. Typical LAESI mass spectra from Allium cepa bulb and Citrus aurantium leaf (data not shown) epidermal cells produced between 300 and 550 peaks. Subpopulations were identified as non-pigmented and pigmented cells for A. cepa, as well as oil gland and regular epidermal cells for C. aurantium. Finding the biomarker candidates for the different phenotypes in such a large dataset is a time consuming and laborious process. In this study we demonstrated cell-by-cell imaging and tested the utility of a multivariate statistical method, orthogonal projections to latent structures discriminant analysis (OPLS-DA), to identify the metabolites responsible for most of the variance in the spectra of visually identifiable subpopulations.

LAESI mass spectrometry was utilized for ambient metabolomic analysis of A. cepa bulb epidermal cells and C. aurantium leaf oil gland cells by ablating single cells and small cell populations, respectively. The cellular heterogeneity within the tissues was successfully preserved in the LAESI mass spectra. The cell-to-cell variations of metabolite concentrations in non-pigmented and pigmented subpopulations of A. cepa cells were represented on a false color scale to produce a cell-by-cell molecular image of the tissue. For example, the distribution of cyanidin ions, which is responsible for the purple pigmentation of some cells, correlated well with the color of cells in the optical image. The variations between different subpopulation of cells were explored by using OPLS-DA on the LAESI mass spectra. The metabolites suggested by OPLS-DA are biomarker candidates that require further verification.

Synthesis and Analysis of Polymers With High Permeabilities and Permselectivities for Gas Separation Applications

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Funding:	$120,000

This project focuses on rational discovery and development of robust crosslinked polyimide membrane materials for energy-efficient purification of natural gas. We worked on the following areas: (1) design and synthesis of 6FDA-based polyimides with comparable chemical structures, (2) thermal properties and chemical structures of the polymers, (3) CO_2-induced plasticization response vs. chemical structure of the polymers, (4) gas separation properties vs. chemical structure of the polymers, (5) sub-Tg thermal cross-linking of the polymer membranes, and (6) physical aging and CO_2 exposure on gas permeation properties of thin films.

We designed and synthesized 6 kinds of 6FDA-based polyimides, which have related and comparable chemical structures. These polyimides were chosen to clarify relationships among the polyimide chemical structures and gas permeability, selectivity, crosslinking, as well as plasticization response.

The chemical structures and thermal behavior of the above synthesized polymers were studied and documented in detail. The thermal behaviors of chemical (with diol) cross-linking (PDMC-PI) and decarboxylation-induced thermal cross-linking of 6FDA-DAM:DABA were investigated. The Ag+ substitution reaction of 6FDA-DAM:DABA was also studied by thermal analysis to explore the feasibility of decarboxylation at lower temperature.

CO_2-induced plasticization response vs. chemical structure of the polymers was investigated by using above synthesized polyimides membranes without cross-linking. The plasticization pressures (where upturns in permeability occur) of the polyimides are tested with CO_2, the most aggressive penetrant in the experiments. And the results were connected with the chemical structures of polymers.

Gas separation properties vs. chemical structure of the polymers were studied by using pure gases (He, O_2, N_2, CH_4, and CO_2) and mixed gas (CO_2/CH_4 with 10% CO_2 and 50% CO_2, respectively) with the membranes without cross-linking. Results were connected with the chemical structures of polymers.

Sub-Tg thermal crosslinking of 6FDA-DAM:DABA polyimide membrane was developed, and was extended to crosslink hollow fiber membrane to alleviate the negative impact of high temperature on the skin and porous substructure of a hollow fiber membrane. Results from both pure gases and mixed gases indicate that the Sub-Tg thermal crosslinking is an effective method in getting plasticization-resistant polyimide membranes.

Physical aging and CO_2 exposure on the gas permeation properties of ultra-thin films were carried out using 6FDA-based thin polyimide membranes. Responses of the materials to various CO_2 pressure profiles were examined along with their aging behavior monitored by permeability measurements.

Cyanometallates, Their Cages, and Associated Host-Guest Behavior

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First generation models of the newest hydrogenase Hmd were prepared in the form of $Fe(SPh)(Ph_2PC_6H_4CO)(CO)_3$ via oxidative addition of thioesters to Fe(0). The structure of this monoiron derivative compares well with the structure of the C176A mutant of Hmd. The derivative $Et_4N[Fe(SPh)(Ph_2PC_6H_4CO)(CN)(CO)_2]$, which, unlike the tricarbonyl, is stable with respect to loss of CO (as also seen for the cyanide-inhibited enzyme, Hmd^{CN}) exhibits IR spectrum that closely matches that of the cyanide-inhibited Hmd. The cyanide was further characterized by X-ray absorption spectroscopy at SLAC further securing the assignment of a ferrous center in Hmd. The pathway for the oxidative addition of the thioester to Fe(0) was illuminated and other Fe(II) acyls were prepared by the oxidative additions of the first diphosphine-functionalized carboxylic acid anhydride.

Since pyridone facilitated proton-transfer is implicated in the action of Hmd we examined the catalytic behavior of Cp*Ir(2-hp)Cl (hp = pyridonate anion) for the “acceptorless” dehydrogenation of secondary alcohols. When monitored in situ, initially formed is the previously unobserved hydride $[Cp^*_2Ir_2(\mu\text{-}H)_2(\mu\text{-}2\text{-}hp)]Cl$, which reverts $Cp^*Ir(\kappa^2\text{-}2\text{-}hp)Cl$, the active catalyst.

Two parallel reaction schemes were developed in the previous contract period. One is termed protonation-induced Lewis acidity (PI-LA) and the other is oxidation-induced Lewis acidity (OI-LA). In PI-LA, 16 e^- metal amido complexes, of the sort used in transfer hydrogenation, are protonated at nitrogen. The resulting cationic 16 e^- center is highly Lewis acidic, even torward H_2 (but not water). OI-LA is operative when the starting complex is formally coordinatively unsaturated and contains an amido-based non-innocent ligand (NIL), such as an 2-amidophenolate. Since the π-donor orbitals of 2-amidophenolate complexes are also the redox-active orbitals (HOMO). Ligand-centered oxidation would be expected to enhance the Lewis acidity at the metal by simultaneously raising the formal positive charge on the complex *and* weakening the metal-ligand π-bonds.

Binding Anions Selectively With Modular Triazolophanes and Releasing Them With Light

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Funding:	$125,000

There are two main objectives for the research involving (1) the basic studies of oxyanion binding and (2) the photodriven release of anions. Good progress has been made on both topics in FY 2011 to date.

OBJECTIVE 1: BASIC STUDIES OF TRIAZOLOPHANE-OXYANION BINDING

We are making progress towards the synthesis of expanded triazolophane-based receptors, which have the larger size required for tetrahedral oxyanions. Synthetic progress towards key naphthalimide building blocks has been established with a new high-yielding synthetic route. Model receptors have been synthesized and they show the naphthalimides turn on anion binding. These experimental suggestions were supported by high-level DFT in collaboration with Raghavachari (Indiana University). They show naphthalimide have activated CH H-bond donors for binding anions just like triazoles. Therefore, naphthalimides represent a new addition to the field and a continuation of our group's efforts in understanding CH H-bonding. The expanded triazolophanes have recently been made on a test scale and will be our next topic of study.

The energetics, stoichiometries and structures of the anion-receptor systems that emerge from titrations conducted in organic solvents like dichloromethane have been characterized for the first time in the field. Most studies overlook the impact of multiple equilibria, such as ion pairing, or only address it qualitatively. We identified these effects as well as protocols to characterize them. We also made increasing use of conformation analyses that could only be possible when using DFT to treat the system. Not only were the enthalpic factors ascertained using theory but also the entropy, thus enabling us to determine an entropy-enthalpy compensation effect when comparing two macrocyclic receptors.

We have also inspected the binding of the rigid parent triazolophanes to cyanide. More to the point, theory was used in a predictive manner to suggest the binding mode and energy. The latter was tested experimentally and verified the predictions.

OBJECTIVE 2: BASIC STUDIES ON PHOTOSWITCHABLE TRIAZOLOPHANES

In this overarching theme, the goal is to bind and release anions using light both when and where we like, as well as to study the basic mechanism of action. In the last period (FY 2010), we have published an account of a proof-of-principle foldamer. In the new period we have created three more in a series as a means to both test the mode of action as well as to improve the performance of the binding and release. We will soon submit a full paper detailing the results. Significantly, this is the first study of its kind in the field of anion recognition where the mechanism of action is clearly shown and understood. We note that two other papers on this topic have appeared since our one in JACS indicating the growing interest in the ability to switch a receptor on and off.

Elucidation and Reduction of Interference Effects in Inductively Coupled Plasma Spectrometry

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The main focus of our efforts in the past was to elucidate the fundamental origins of matrix interferences that occur in plasma-source emission and mass spectrometry. That topic still occupies an appreciable fraction of our time. However, upon urging by DOE-BES staff, we are branching out into new areas, especially into a new field termed “ambient mass spectrometry, to which we can profitably apply many of the experimental methods and fundamental understandings that were employed in our earlier work. In particular, our exploration of alternative plasma sources led us in the direction of a flowing afterglow. Our earlier fundamental studies into conventional glow discharges demonstrated that they can be sustained stably (but unconventionally) even at atmospheric pressure. Of course, at atmospheric pressure, the conventional structure of a glow discharge changes tremendously and is being investigated in detail in our laboratory. Early on, we found that sample solutions and sample vapor could be introduced into an atmospheric-pressure glow discharge but at the cost of precision and sensitivity. The problem, of course, is that the sample perturbed the relatively low-power discharge and promoted both matrix interferences and loss of sensitivity. We therefore turned to use of a flowing afterglow, one in which the discharge products were allowed to exit the discharge chamber and only then to encounter sample species. In this configuration, the sample material cannot influence the discharge, since it never interacts with it.

Our initial foray into the use of the flowing atmospheric pressure glow discharge was to use it for ionization of compounds in the gas phase. Vapors of a number of substances were introduced into the flowing afterglow and their mass spectra determined. To our surprise, the discharge effluent not only ionized species with great efficiency, but also produced very little molecular fragmentation. The resulting spectra were therefore extraordinarily simple, consisting mainly of either the protonated molecular ion or the molecular ion itself. Indeed, the spectra were so uncluttered that we found it possible to identify all the constituents in simple mixtures, even without prior separation. We therefore engaged in a study to characterize the ionization mechanism in greater detail, something that still occupies a fair fraction of our time. At present, it appears that molecules having a substantial gas-phase basicity are ionized most efficiently by proton transfer from protonated water clusters generated by interaction of atmospheric constituents with the flowing afterglow. In contrast, compounds with a lower gas-phase basicity, or those of very low polarity, are more commonly ionized by charge transfer from species such as $N2^+$ or NO^+ ions, generated by a sequence of reactions initiated in the flowing afterglow.

Later, the flowing atmospheric-pressure afterglow (FAPA) was found to be useful not only for the ionization of gas-phase molecules but also for the desorption and ionization of solids. As with our studies involving sample vapors, our understanding of the desorption process lags behind the demonstration of its practical attributes. At present, however, it appears that desorption is primarily thermal in nature. As in the case of vapor-phase samples, solid materials can be not only volatilized but also ionized by the FAPA and produce surprisingly simple spectra, consisting again of either the molecular ion or protonated molecular ion. Because ionization occurs directly in the ambient atmosphere, this new spectrometric source appears to be highly attractive for the “real world” analysis of samples of many kinds. To date, detection limits in the femtomole regime have been determined for a range of sample materials, including drugs of abuse, pharmaceutical products, compounds of forensic interest, biological tissues, and even solution samples directly.

We have sought not to restrict our AMS investigations to only our own FAPA source, but to examine the utility and fundamental characteristics of other ambient mass spectrometry sources as well. One promising such source is the so-called "low-temperature plasma probe" (LTP), which is based on a helium dielectric-barrier discharge. Unlike FAPA, the LTP operates with a high-voltage (~2 kV), low-power (~2 W) ac (~2kHz) discharge, and employs an electrode arrangement that prevents electrode interaction with the discharge. Because of its low power, the plasma plume issuing from the LTP is so cool that it can be used on living tissues, yet produces measurable spectra from many samples. In our first investigation of the LTP source, we applied many of the same spectroscopic diagnostics that we formerly used with the inductively coupled plasma. In particular, we employed our spatial imaging spectrometers to map reactive species in both the LTP plasma and in its afterglow. From these maps, the origin of impurities important in practical mass-spectrometric analyses, such as H_2O, N_2, and O_2 was deduced. We next utilized Boltzmann plots of OH-radical optical-emission spectra to determine rotational temperatures and found them to be roughly 280K within the dielectric-barrier discharge and to rise gradually to about 320K outside the discharge chamber. Presumably, the rise in temperature is the result of "thermalization" of the discharge products through interaction with molecular gases in the atmosphere. Electron number densities in the LTP were measured by means of Stark broadening of the hydrogen-beta emission line and yielded values of roughly 10^{13} cm^{-3}. This value and the OH rotational temperatures are consistent with what others have measured for dielectric-barrier discharges.

We next turned to an elucidation of reaction mechanisms responsible for formation of the afterglow and reagent ions in the LTP. Interestingly, and in contrast with unwarranted assumptions made by others in the literature, we found that the dominant positive ion in the LTP plasma is He^{2+} rather than He^{+}, and that it is He^{2+} that serves to carry energy from the plasma into the open atmosphere. There, He^{2+} interacts with atmospheric N_2 to form N_2^+, which is an important reagent ion and one of the key reaction intermediates for the formation of other reagent ions, such as protonated water clusters. We also compared rotational temperatures of the LTP afterglow for both N^{2+} and OH as thermometric species and found a strong discrepancy between the two sets of values. The origin was discovered to be non-thermal excitation of N_2^+ by charge transfer from He_2^+. The consequence was that OH yielded rotational temperatures that were statistically identical to that of the ambient atmosphere, whereas N_2^+gave values that were as much as 250K higher. One origin of excited He in the LTP afterglow is from dielectronic recombination of vibrationally excited He_2^+ ions.

During the coming year, these fundamental investigations will be expanded by developing a fluid-dynamics model to characterize the FAPA afterglow. These theoretical studies will be bolstered by schlieren measurements to map the true flow and to reveal how the FAPA afterglow plume interacts with sample surfaces. We intend also to explore the practical potential of the FAPA by coupling it to laser ablation. Laser ablation is known to generate nanoparticles of even the most refractory of solid surfaces. Such nanoparticles should be amenable to analysis by AMS sources, particularly the FAPA.

Molecular-Level Investigation of Diffusion Behaviors within Cylindrical Nanoscale Pores

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Funding:	$240,000

The primary objective of this project is to develop a quantitative understanding of molecular mass transport within microcapillary-supported, cylindrical nanopores having well-defined diameter (2-40 nm), alignment and surface chemistry. The mass transport of individual probe molecules within the nanopores is being investigated by state-of-the-art single-molecule fluorescence techniques such as single molecule tracking (SMT) and fluorescence correlation spectroscopy (FCS). Single molecule mass transport data will be compared to ensemble flux data obtained from identical nanopores. Use of well-defined cylindrical nanopores allows for direct comparison of experimental results with theoretical models. A comprehensive understanding of molecular mass transport behavior within nanoporous media will be obtained, and will aid in the engineering of nanoporous media optimized for applications in chemical separations and catalysis.

During the first two years of this project we, (1) developed a simple, quantitative method to assess nanopore alignment based on the analysis of one-dimensional motions exhibited by single molecules in SMT studies (K. H. Tran Ba, et al. *Phys. Chem. Chem. Phys*. 2011, 13, 1827; (2) applied this same method for assessing flow-induced alignment and diffusion pathways in rod-shaped block copolymer micelles (A. W. Kirkeminde, et al. *J. Phys. Chem*. B 2011, 115, 12736); (3) analyzed the influence of aging time on the flow-induced alignment of micelle-templated mesoporous silica channels (S. C. Park, et al., in preparation); and (4) studied the effect of organic solvent evaporation on the alignment of cylindrical domains in block copolymer films (K. H. Tran Ba, et al., in preparation). In addition, using ensemble techniques we have (5) clarified the surface chemistry of cylindrical nanopores derived from polystyrene-polymethylmethacrylate diblock copolymers (S. Ibrahim and T. Ito, Langmuir 2010, 26, 2119.; F. Li, et al., RSC Adv., DOI:10.1039/C1RA00471A.); (6) demonstrated solvent-induced control of effective pore diameter with electrochemical impedance spectroscopy (D. M. N. T. Perera, et al., Langmuir 2011, 27, 11111.); (7) clarified hindered diffusion of cytochrome c within the nanopores on the basis of electrochemical data and finite element computer simulations (B. Pandey, et al., Electrochim. Acta, 2011, 56, 10185.); and (8) assessed microcapillary-incorporated monoliths by conductance and flux measurements (S. Ibrahim, et al., in preparation). Seven students (five graduate students, two undergraduates) and one postdoctoral associate have worked on the project to date.

Hyper-Thin Membranes for Hydrogen Purification

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Funding: $140,000

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 “hyper-thin (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 hyper-thin 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.

In a broader context, the new surface modification technique that will be developed is expected to provide a mild alternative to conventional surface treatment methods (e.g., oxidation with ozone, $KMnO_4$, etc.) which usually produce complex mixtures of functional groups. Because of the importance of surface structure and composition for controlling properties such as wetting, weathering, adhesion, dye adsorption, friction, permeation, biocompatability, etc., the “adsorption/gluing” approach that will be developed (i.e., where polymeric surfactants will be adsorbed onto hydrophobic surfaces and crosslinked with polyelectrolyte counterions) should find use in a variety of applications. In addition, the structurally matched polyelectrolytes that will be synthesized are expected to afford hyper-thin films of exceptional H_2/CO_2 permeation selectivity, or exceptional CO_2/H_2 permeation selectivity when poly(ethylene oxide)-based polyelectrolytes are used.

Chemical Microscopy of Conjugated Macromolecular Systems: Fundamental Design Strategies for Nanoscale Photonic Antennae and Networks

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Funding: $129,000

Over just a few years, Chemical Microscopy - as a tool for optical interrogation of organic semiconductors - has evolved as a powerful technique to elucidate fundamental mechanisms and timescales for energy and charge transport processes in a variety of chemical systems. Understanding the molecular-level details of these processes is critical to the development of robust and efficient organic-based optoelectronic and solar energy harvesting applications. In this renewal proposal, we describe new directions in analytical chemical imaging of nanostructured organic semiconductors relevant to next-generation energy harvesting devices. In our work, we showed how a chemical microscopy approach combining scanning probe microscopies with detailed analysis of polarization, wavelength, and time-correlations of emitted photons can be used to recover important structural and dynamical information on conjugated molecules and nanostructures. Our proposed work described for the renewal period builds on this expertise and seeks more detailed spatially-resolved photophysical information using a combination of both far-field fluorescence, nanoparticle Raman, and near-field scanning probes. Of particular interest is the chemical microscopy of poly-3-hexyl thiophene (P3HT), and associated polymer blends under 3-dimensional nano- confinement. This is a chemical system that is attracting a great deal of interest in the polymer-based photovoltaic communities. The chemical information obtained from our proposed experiments will address important fundamental questions of the role of molecular architecture and film morphology of semiconducting polymers, and provide valuable feedback to synthetic chemists and polymer-based device engineers for enhanced optoelectronic performance and energy harvesting efficiency.

Separations of Stable Isotopic Ions in Homogeneous, Highly Charged Nanopores

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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. During the past year, research focused on modifying membrane nanopores through alternating deposition of poly(styrene sulfonate)/protonated poly(allylamine) (PSS/PAH) bilayers. For 50 nm pores, the pore radius decreases 5-10 nm after deposition of each bilayer to provide control over the pore size. However, the K^+/Mg^{2+} transport selectivity of the membranes reaches 10 after deposition of 2 bilayers and then declines, perhaps because the charge density decreases as the polyelectrolytes become more constrained in the nanopore. Remarkably, in bare membranes with 30 nm pores adsorption of a single PSS/PAH bilayer leads to K^+/Mg^{2+} transport selectivities as high as 100. The selectivities decline with increasing ionic strength, consistent with a selection mechanism that involves strong electrostatic exclusion of the divalent ion from the positively charge membrane pores. (The high positive charge is present in the pore because the polycation is the terminal polyelectrolyte.) Future work will examine whether the development of streaming potentials across these membranes can facilitate separation of ions with similar mobilities. Control over surface charge and pore size is essential for such separations.

Related studies examined the transport of anions and cations through polyelectrolyte multilayers. Because these films are more permeable to anions than cations, salt transport through such membranes results in membrane potentials that affect transport properties. In particular, these potentials can lead to higher concentrations of trace ions in the permeate than in the feed. Such “negative rejections” may allow recovery of acid or trace ions from contaminated solutions. An understanding of the anion/cation permselectivity of membranes is vital to predicting their separation performance.

Interfacial Solvation Under Aggressive Conditions

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Funding: $135,000

We are developing a molecular-level understanding of the microenvironment, fluidity, and dynamics within separation membranes based on organosilanes, polyimides, poly(benzoxazoles), poly(dimethyl siloxanes), and poly(ethylene) oxides under aggressive conditions. Specifically, we are developing carefully designed silica-based interfaces that are derivatized with well-defined segments (e.g., alkyl, perfluoroalkyl, poly(ethylene oxide) (PEO), poly(dimethylsiloxane) (PDMS), and aromatic polyimides (PI)), strategically positioned fluorescent reporter molecules, and used steady-state and picosecond time-resolved total internal reflection fluorescence spectroscopy to elucidate how and why the interfacial microenvironment, fluidity, and dynamics are influenced when contacted with pure gases (e.g., CO_2) and relevant gas mixtures (e.g., CO_2/H_2, CH_4/n-C_4H_{10}) across the gas, supercritical, and liquid region (i.e., under aggressive conditions that are relevant to a practical separation).

Coordination-Chemistry-Derived Materials Featuring Nanoscale Porosity and Selective Chemical Separation

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Funding: $220,000

The objective of this project is to develop new materials capable of separating gas mixtures important to DOE, including hydrogen/methane, nitrogen/methane, CO_2/methane/water, Kr/Xe, acetylene/methane, and acetylene/CO_2 mixtures. These and similar gas separations are often performed using energy-intensive cryogenic distillation. It has long been recognized that selective adsorption in porous materials could be used as an energy-efficient alternative, but materials with the requisite selectivity, capacity, and stability have not been available. We are taking advantage of significant, recent advances in materials chemistry and computational modeling to develop new materials suitable for use in pressure-swing adsorption and related separation processes. In particular, we are focusing on nanoporous metal-organic frameworks (MOFs), which are synthesized solvothermally from molecular building blocks (organic struts) and metal ions (constituting nodes) held together by moderately strong coordination bonds.

We are using a two-pronged approach. The first prong is “hypothesis driven” and exploits recent advances in our labs in MOF synthetic chemistry. Conceptually new approaches to small-molecule separation have been, or will be, developed and evaluated by enlisting MOFs that (1) present transition-metal ions having very low coordination numbers, (2) contain high-capacity, chemically-tailored cavities, or (3) feature large, cross-cavity electric fields. The robustness of MOFs, along with the ability to tailor them by choice of building blocks or in a post-synthesis fashion, allows for the creation of functional adsorption sites that cannot be synthesized in molecular or supramolecular environments or other nanoporous materials such as zeolites. We hypothesize that these sites and environments, which are thus far unique to materials developed at Northwestern, can be exploited in small-molecule separations. The project will develop new materials, test them for important separations, and improve our fundamental understanding of adsorption selectivity.

The second element of the proposed investigation focuses on high-throughput computational screening of MOFs for chemical separations. We are implementing an ambitious plan to generate millions of MOFs in silico and to screen their properties computationally for efficacy in four test-case separations. The plan includes a method for generating the hypothetical MOF structures and for evaluating their properties in a high-throughput manner. The building-block nature of MOF chemistry, together with our experience in synthesizing, purifying, and stabilizing MOFs, ensures that many of the structures discovered in this way can be synthesized and evaluated experimentally. The hypothesis-driven approach and high-throughput computational screening approach are complementary and are functioning in tandem.

Molecular Aspects of Transport in Thin Films of Controlled Architecture

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Funding:	$155,000

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 problems in 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., then generate control signals that control transport based on those characteristics.

Based on an understanding of transport and reactivity in nanoscale architectures, microfluidic and nanofluidic structures may be combined to achieve integrated microfluidics, i.e., structures capable of handling small fluid samples at unprecedented volumes. 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 nanocapillaries. Development and application of novel nanoscale measurements is needed to determine the fundamental chemical and physical factors that determine how transport couples to reactivity under conditions of confinement and crowding in nanopores and nanochannels. Single molecule studies of translational and rotational dynamics are being pursued in single nanopores under electrokinetic (EK) flow where the degree of confinement is systematically varied. In addition, wide-field single molecule tracking is used to follow translational motion, in systems where the degree of molecular crowding is systematically varied. 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. These structures allow the following questions to be addressed: (a) model electrochemical reactions are studied as a function of flow conditions, pore geometry and electrochemical driving force; (b) enzymatic catalysis are studied with covalently immobilized oxidases and oxidoreductases of interest in electron shuttling applications; and (c) catalytic reactions are modeled using the Pd-catalyzed reduction of small oxyanions relevant to environmental remediation. 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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This research is aimed toward exploiting developments in two and three dimensional imaging mass spectrometry. This unique technique allows the chemistry of small molecules in the near surface region of a solid to be mapped with a lateral resolution of a few hundred nanometers, and a depth resolution of about 10 nm. The basic idea is to utilize an energetic cluster ion beam, consisting of C60 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. This instrumentation will be utilized in a number of fundamental studies aimed at determining the chemical composition of aerosol particles associated with the environment, and will emphasize the study of biological particles at the single cell level to provide insight into the mechanism of how algae produce organic molecules that could be used as biofuels.

Mechanistic Studies of Activated Hydrogen Release from Amine Boranes

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Funding:	$300,000

Effective hydrogen storage is one of the most significant technical barriers to the successful implementation of the hydrogen economy. Owing to its high hydrogen content (19.6 wt%) and recently demonstrated regenerability, ammonia borane (AB) continues to be one of the most promising materials for a chemical-hydride based hydrogen storage system for transportation applications. Our work has demonstrated that ionic liquids, base-initiators and/or metal-catalysts can each significantly increase both the rate and extent of AB H_2-release. Our studies have further shown that depending upon the activation method, AB H_2-release can occur by very different mechanistic pathways and yield different types of spent-fuel materials. The goal of our project is to develop a fundamental understanding of these H_2-release mechanisms and to elucidate the important controlling factors for each type of reaction. Such detailed understanding is vital to the continued discovery and optimization of chemical-hydride based H_2-release systems. Some highlights from last year's work are briefly described below:

Our ongoing studies of the activating effect of bases on the rate and extent of AB H_2-release led to the syntheses and characterizations of new 5- and 7-membered borane-capped anionic aminoborane oligomers, $[H_3BNH_2BH_2NH_2BH_3]^-$, $[H_3BNH_2BH_2NH_2BH_2NH_2BH_3]^-$ and $[HB(NH_2BH_3)_3]^-$, that are likely early intermediates in base-promoted AB H_2-release. X-ray crystal structure determinations suggest that sequential H_2-elimination reactions leading to chain growth are likely facilitated by N-H--H-B dihydrogen bonding interactions between the AB N-H protonic hydrogens and the hydridic B-H hydrogens of the growing anionic aminoborane chains. These results provide the first direct support for an anionic chain-growth mechanism as an initial step in base-promoted AB H_2-release reactions.

Complementing and extending our earlier studies that demonstrated that ionic liquids (ILs) activate AB H_2-release, we demonstrated in the last year that metal catalyzed AB H_2-release can also be achieved in ILs, with a wide range of pre-catalysts giving enhanced initial rates at temperatures below that required to enable IL promoted pathways. This is significant since liberation of both heat and H_2 at relatively low temperatures via metal mediated pathways may increase the efficiency of IL-promoted release of additional hydrogen. For example, rapid metal-catalysed AB H_2-release at 75°C (a temperature that can be obtained from fuel cell waste heat) could raise the temperature of the liquid IL-AB fuel above 110°C at which point the rate and extent of IL-promoted H_2-release have been shown to approach DOE targets. We also showed that the nature of the IL can have a profound influence on both the selectivity and mechanistic pathways of metal-catalyzed AB H_2-release. Additional studies with a variety of catalysts, including newly developed Fe and Mn complexes, are currently underway in both IL and conventional solvents, along with investigations of the chemical reactivity of isolated intermediates, such as a unique AB-analog of ethylcyclobutane, are currently underway.

The Development of Nano-Composite Electrodes for Natural Gas-Assisted Steam Electrolysis for Hydrogen Production

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Funding:	$300,000

We are studying the chemistry of oxide-oxide interfaces in the air and fuel electrodes of both solid oxide electrolyzers (SOE) and fuel cells (SOFC), with the goal of determining how interactions at these interfaces affect electrode microstructure and electrochemical function. The insights are obtained through detailed studies of model electrodes consisting of thin films of active perovskite components on yttria-stabilized zirconia (YSZ) single crystal surfaces, along with studies of actual working electrodes that are synthesized using infiltration methods developed in our lab. For air electrodes, we are using concepts from the fundamental studies to develop methods for stabilizing the microstructure of active perovskite components through the use of nanometer-thick, oxide interlayers and by using chemical vapor deposition (CVD) and layer-by-layer (LbL) deposition to build well-defined layered structures within porous YSZ electrode scaffolds. New electronic conducting oxides are being explored as possible current conducting components in fuel electrodes; and we will develop methods, such as the use of core-shell catalysts, to produce thermally stable catalysts for these electrodes.

Electrohydrodynamic Tip Streaming

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Funding:	$135,000

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 goal of this research program is to develop a fundamental understanding of the temporal development of EHD tip streaming phenomena.

One reason why a fundamental understanding of EHD tip streaming had heretofore been elusive is the existence of the large disparity in length scales between the macroscopic drops/films and the microscopic/nanoscopic jets that emanate from the conical tip structures. In this research, computation and experiment are being used in concert to investigate EHD tip streaming from liquid drops and films of finite conductivity. A main accomplishment of this work has been the demonstration by careful simulations that EHD tip streaming does not occur if the liquid is perfectly conducting or perfectly insulating, as had been assumed in almost all previous studies. Another major accomplishment has been the successful performance of the first set of simulations in which it has been possible to calculate not only the emitted tip streaming jets but also the drops that are shed from their tips. Through such calculations, we have been able to determine theoretically the sizes and charges carried by the emitted electrospray drops. We have already shown that contrary to conventional wisdom, there are multiple scaling laws governing drop size and charge. Two current challenges being tackled include the following: (1) First, as the conductivity of the liquid increases, the sizes of the emitted drops decrease. (2) Second, if the parent drops bear net charge, the emitted jets are longer than those in situations in which the parent drops are uncharged. Both of these issues exacerbate the multi-scale nature of the problem being tackled. Moreover, drop size and charge appear to follow different scaling laws when the parent drop is uncharged and when it is.

An important scientific question is the relationship between tip streaming in EHD and tip streaming in other physical problems. We had already investigated this relationship earlier in the case of dripping-jetting transitions when two liquids flow out of two concentric nozzles. We have recently discovered and have started studying a yet closer analog to EHD tip streaming than a two-liquid co-flow. This closer analog is referred to as the transition from selective withdrawal (SW) to viscous entrainment (VE). As in EHD tip streaming, the SW to VE transition is also replete with multiple scaling laws. We have already discovered that some of the heretofore theoretically predicted scaling laws may in fact be suspect.

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? Quite recently, we have successfully studied the equilibrium shapes and stability of such electrified double droplet systems (DDSs). We are now poised to study the dynamics of such DDSs, including EHD tip streaming from their tips.

Preparation of Chemically Functionalized Surfaces through Ion Soft Landing and their Utilization in Heterogeneous Reactions

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The overall objective of this work is to prepare surfaces with appropriate chemical functionalities via soft landing (SL) of molecular or cluster ions. Two new capabilities, in-situ Raman and temperature programmed desorption, were successfully implemented in the soft landing instrument. Their utilization in investigating functionalized surfaces prepared through ion soft landing was also achieved in FY 2011.

INSTRUMENT MODIFICATION

The SL instrument at Purdue can be used to mass-select particular ions and deposit them at a selected low energy onto a selected surface in high vacuum. The modified surface can be characterized by in-situ secondary ion mass spectrometry (SIMS). Now the system has been further modified to add new capabilities that include (1) a new high vacuum compatible, low cost in-situ Raman analysis capability with 2D imaging provisions and (2) the ability to expose the characterized surface to vapor phase reagents and perform temperature programmed desorption (TPD) analysis in-situ.

The vacuum chamber for in-situ Raman measurements is attached perpendicular to the fast entry chamber of the SL instrument. The advantage of the design is the fact that all measurements can be conducted without breaking vacuum and hence one achieves analysis of modified surfaces in their native form. Following SL any combination of in-situ Raman and in-situ SIMS can be performed. In-situ 2D Raman spectral imaging was achieved with the help of the manual micrometer XYZ stage.

The combined capabilities of SERS and SIMS, two powerful characterization tools in a single instrument fitted with in-vacuum sample transport capabilities, facilitates in-situ analysis of surfaces prepared by ion SL.

CHEMICALLY FUNCTIONALIZED SURFACES

With the new instrumentation and characterization tools, we have studied a number of systems with emphasis on determining the charge state of the deposited ions. Cations/protonated ions derived from Rhodamine 6G, crystal violet, methyl red, peptides and negative ions derived from fluorescein, copper phthalocyanine and methyl orange are soft landed onto various surfaces and investigated using SERS and SIMS. Well-defined SERS features are observed in as little as 15 min of ion deposition, and SIMS in even less time. For example, in the case of Rhodamine 6G, deposition of ~3 pmo1 gave high quality SERS spectra with the spectroscopic responses being derived from just ~0.5 fmol of material. The high sensitivity of SERS allows rapid and molecularly specific detection of soft landed species. Characteristic changes occur in Raman features when Rhodamine 6G is deposited under conditions that favor gas-phase ion fragmentation. Simultaneous deposition of both the intact dye and its fragment ion occurs and is confirmed by SIMS analysis. Deposition of crystal violet cation at higher landing energies results in fragmentation and a hydrogen abstraction reaction in its dimethyl amino group at the surface. Above 40 eV landing energies, a band due to NH_2 stretching vibration (1640 cm-1) emerges as a result of dissociation and surface reaction. Corresponding SIMS spectra have peaks at m/z 358 and m/z 344 due to the surface fragmentation. In the case of methyl red, SERS features suggest that the protonated from is retained at the surface. The study was extended to other Raman active surfaces, including Au nanostar and Au coated Ni nanocarpet surfaces. Alternatively, high quality SERS data could be obtained by spin coating a silver colloid solution over the modified surface once SL is complete.

Reactive landing is used to tailoring surfaces with biomolecules for the preparation of biosensors and substrates for cell adhesion. Lysine containing peptides are successfully attached to dithiobissuccinimidyl nitrobenzoate (DSNB) surfaces. The difference in bands at 1553 cm-1, 1329 cm-1 and 1079 cm-1 (of DSNB) confirms the occurrence of reactive landing. The absence of Lys-Phen molecular ion and a fragment appeared at m/z 277 in the SIMS data also support the reactive landing event.

Superior carrier mobility of inorganic materials and the processability of organic materials could be combined in organic-inorganic hybrid materials. Graphene oxide (GO) is a 2D nanomaterial with interesting electrical and chemical properties. We modified thin films of GO with functional molecules such as copper phthalocyanine and porphine using the SL procedure. This route has advantages over solution phase methods as the structure of the GO film could be preserved at the surface and the desired chemical patterns could be generated on the surface. In-situ SERS and SIMS data show successful modification of surfaces with molecular species through non-destructive deposition. These and other results suggest ion SL is effective in chemical modification of surfaces and the in-situ SERS and in situ SIMS provide complete characterization of surfaces produced by ion SL.

TEMPERATURE PROGRAMMED DESORPTION (TPD)

Apart from in-situ Raman, a TPD capability has been added to the SL instrument and its performance evaluated. This will help to analyze products of gas phase-surface interfacial reactions. The system includes a heating-cooling dock with liquid nitrogen circulation, residual gas analyser (RGA), and appropriate sample transfer systems. An ongoing experiment is the preparation of an organometallic catalyst surface through SL and use of this surface for ethylene epoxidation.

The Dynamics and Thermodynamics of Gaseous Macro-ions

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This project is devoted to understanding chemical and physical processes associated with molecular mass spectrometry with an overall objective of enhancing the value of mass spectrometry as a structural tool in the support of the DOE missions. Mass spectrometry is a powerful tool that has become essential in all of the atomic and molecular sciences that comprise the DOE research mission. It's value derives from the ability to determine atomic and molecular mass with accuracies far greater than any other method, the quantitative measurements that can be made based on relative signal strengths (e.g., in the measurement of isotope ratios), and the structural information regarding polyatomics species that can be obtained from the chemical and physical behaviors of ions.

Currently, emphasis in this work is placed on methods for dissociating ions that lead to structural information and the reactions of oppositely charged ions as means for manipulating ion identities in structurally informative ways. Dissociation approaches include collisions of ions with gaseous atoms/molecule, collisions with surfaces, and photofragmentation. Ion/ion reactions have focused principally on the two common reaction types in chemistry, viz., proton transfer (i.e., acid/base chemistry) and electron transfer (i.e., oxidation/reduction chemistry). Very recently, we discovered several ion/ion reactions that lead to selective covalent bond formation. This line of work opens up new vistas for applications of tandem mass spectrometry because it implies that the enormous range of useful chemical reactions that take place in solution may be accessible as reactions in tandem mass spectrometry. If so, altogether new kinds of experiments can be envisioned that may solve some of the many difficult structural characterization problems that currently cannot be addressed by conventional fragmentation chemistries.

Combinatorial and High Throughput Membrane Synthesis and Testing: Tailoring Membrane Surfaces to Applications

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Three critical aspects of searching for and understanding how to find highly resistant membrane surfaces to protein adhesion are addressed here with specific application to synthetic membrane filtration: (1) the discovery of a series of previously unreported monomers from a large library of monomers with high protein resistance and subsequent low fouling characteristics for membrane ultrfiltration of protein-containing fluids, (2) the development of a new approach to investigate protein-resistant mechanisms from structure-property relationships, and (3) the adaptation of a new surface modification method, called atmospheric pressure plasma-induced graft polymerization (APP), together with a high throughput platform (HTP), for low cost vacuum-free synthesis of anti-fouling membranes. Several new high- performing chemistries comprising two polyethylene glycol (PEG), two amines and one zwitterionic monomers were identified from a library (44 commercial monomers) of five different classes of monomers as strong protein-resistant monomers. Combining our analysis here, using the Hansen solubility parameters (HSP) approach, and data from the literature, we conclude that strong interactions with water (hydrogen bonding) and surface flexibility are necessary for producing the highest protein resistance. Superior protein-resistant surfaces and subsequent anti-fouling performance was obtained with the HTP-APP as compared with our earlier HTP-photo graft-induced polymerization (PGP).

Antenna-Coupled Light-Matter Interactions

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We study light-matter interactions in nanoscale environments. More use ’optical antennas 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 photodetection, light emission, sensing, heat transfer, and spectroscopy.

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) 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 exploring the possibility of antenna-coupled electro-optical transduction, i.e., processes in which electrons are locally converted into photons, and vice vera. We are studying optical rectification at metal-metal tunneling junctions to directly convert incident photons to electrons (optical rectennas) and electron-plasmon coupling to convert tunneling electrons to photons.

Nanoporous Membranes for Hydrogen Production: Experimental Studies and Molecular Simulation

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In this project, we study SiC nanoporous membranes, which show the potential to overcome some of the difficulties other inorganic membranes face, particularly under conditions typically encountered in reactive separations for H_2 production, and in fuel-cell applications. Our previous efforts had focused on the preparation of the SiC membrane supports and the deposition on the substrates of thin nanoporous SiC films by the pyrolysis of pre-ceramic polymeric precursors. These studies have led to the preparation of high-temperature, steam-resistant, hydrogen-permselective membranes. However, the properties of these SiC membranes must be significantly improved before they find practical applications. In this project, we systematically investigate and further develop the technique of pre-ceramic polymer pyrolysis to produce nanoporous SiC membranes and films, which are both cost-efficient and industrially viable. The main focus of our project is on trying to understand the formation process of the membranes, namely, how the initial structure of the polymeric precursor and the pyrolysis conditions impact the final membrane characteristics. Our efforts involve extensive experimentation of the membrane formation process using a variety of in-situ techniques, as well as modeling of the pyrolysis process itself by molecular dynamics simulations, since the understanding must be at the molecular level. The new science that is being developed impacts not only the fabrication of SiC membranes, but also the general field of inorganic membranes including, for example, carbon molecular-sieve and mixed-matrix membranes. A key outcome of our effort will be able to prepare a membrane with certain "optimal" properties (e.g., permeance, separation factor, and surface characteristics) by being able to determine in a systematic way the type of polymeric precursor one needs to use, and the preparation method and procedure that one must utilize. As noted above, in addition to the extensive experimental work required, this needs molecular-level understanding, which necessarily involves MD simulations. The novel SiC membranes under study in this project exhibit good potential for reactive applications for the production of H_2, as well as for fuel-cell applications. In addition to focusing attention on an important class of materials, this project also generates fundamental insight, which will impact the knowledge base of the broader field of transport and reaction in nanoporous media, and is likely to catalyze new thinking and rapid new advances in the area.

A Computational and Experimental Investigation into the Transport Through of Protons near the Electrolyte/Water, Electrolyte/Catalyst and Electrolyte

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In this project we use a variety of multiscale modeling tools to extract structure/property relationships from simulations of proton exchange membranes and the electrode/electrolyte interfaces in membrane electrode assemblies of hydrogen fuel cells. Conventional molecular dynamics (MD) simulations are employed to model the molecular-level structure of hydrated polymer electrolyte membranes. These simulations provide an understanding of the local structure (< 10 Å) pair correlation functions for the atoms in the water, hydronium, and sulfonic acid group of the polymer electrolyte. The MD simulations provide the morphology of the nanoscale aqueous domain that exists in the hydrated membrane. They also provide short-time dynamics of water molecules. Reactive molecular dynamics (RMD) simulations are employed to incorporate the proton hopping reaction for structural diffusion of charge into the simulations. The RMD simulations are capable of capturing the effect of humidity on all three components to the charge self-diffusivity: vehicular, structural, and the correlation of vehicular and structural terms. The short-time mean-square-displacements from the MD simulations are input into mesoscale confined random walk (CRW) simulations to generate statistically reliable self-diffusivities of water in the hydrated membrane as a function of water content. The CRW simulations provide a characteristic dimension of the water clusters as well as the intrinsic self-diffusivity in the absence of poor connectivity of the aqueous domain. The combined MD/CRW results are input into continuum level percolation theories to obtain a predictive model of water and charge transport as a function of the nanostructure of the hydrated membrane.

This multiscale approach, incorporating processes from the quantum scale (proton hopping) to the continuum scale (percolation), generates self-diffusivities in excellent agreement with experimental measurements. It allows us to generate the structure/property relationship between the nanoscale structure of the hydrated membrane and the macroscopic conductivity. Work is currently underway to test the validity of this approach in novel membrane materials and geometries.

Separation of Highly Complex Mixtures by Two-Dimension Liquid Chromatography

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The solution of certain problems requires separation methods far more powerful than those currently available and may be found only in the combinations of two or more different chromatographic and/or electrophoretic separation modes. Unidimensional separations cannot provide a sufficient separation power to resolve the thousand compounds found in metabolomic samples. We propose to apply advanced separation methods 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.

Previous studies led to the choice of four algae species belonging to different families of cyanobacterias: Scenedesmus dimorphus, Prymnesium parvum, Botryococcus braunii, and Chlorella protothecoides. These species were chosen from a list of algae suggested by DOE as having a relatively high yield in lipid production since their dry biomass may contain up to 40% of lipids or more. Significant information on the behavior and physiology of these species is available. At this point we have limited but promising data about the lipid metabolism of the chosen species. The selected organisms produce 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 those compounds by combining two-dimensional chromatography and mass spectrometry. Once these metabolites are known it will be possible to correlate their concentrations and the production of lipids that could be used in diesel fuel. Based on the outcome of this study, current knowledge will permit scientists to increase the metabolism of chosen algae 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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This project focuses on fundamental chemistry and advanced methodologies and techniques that are essential for the continued development and application of structural mass spectrometry (MS). The research focuses on two areas: (1) development of ionization techniques that permit selective and efficient ionization of analytes and (2) rapid, high-throughput analytical methodologies, specifically tandem MS and ion mobility-mass spectrometry (IM-MS), that yield high quality ion structure information. Research area one encompasses several strategies aimed at developing molecular sensors based on the optical and chemical properties of metallic nanoparticles (NP). The strategy utilizes Ag and Au NP, primarily spheres and nanorods (NR), functionalized with various organic molecules. These NP and NR possess electronic transition that overlap with the emission of readily available laser systems (N2 and Nd:YAG lasers), and these wavelengths are also compatible with many analytes of interest. For example, we have shown that AuNR functionalized by 4-amino-thiophenol greatly enhance the laser desorption ionization (LDI) yields for polar small molecules and macromolecules. Similarly, lipid functionalized AuNPs and AuNRs can be used to selectively capture hydrophobic analytes from complex mixtures, i.e., plant extracts and calf serum, and the analytes can then be ionized by LDI and detected by MS. In addition, the surface plasmon resonance (SPR) band of AuNRs can be red shifted by controlling the length of the NR. For example, an AuNR having an aspect ratio (length-to-diameter) of ~10:1 absorbs (SPR band) strongly between 750-900 nm, whereas 5 nm spheres absorb (SPR band) strongly at ~520 nm. Using this strategy we have successfully performed LDI of both small molecules and macromolecules using much longer laser wavelengths, 800-1064 nm. There are two distinct advantages to this strategy: (1) LDI can be performed using low cost diode lasers and (2) the chemical background in the LDI mass spectra is reduced, which facilitates detection of low abundance species, which also enhances our abilities for imaging MS.

Research area two objectives focus on gas phase ion chemistry and instrument development for structural characterization of complex molecules. This area also utilizes enhanced molecular dynamics simulations (MDS) and computation methods for interpretation of the experimental data. Electro-spray ionization (ESI) and variations on this strategy (post-ESI ion-ion and ion-neutral chemistry for charge state changing reactions) are important ionization methods for research area two. Although LDI has played a major role in our tandem MS and IM-MS research, ESI has also proved highly useful for many aspects of the structural MS studies. The Achilles heel of MS is that many molecules exist as isomeric species, which have the same m/z value and oftentimes the mass spectra of these molecules are similar, if not identical. 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, in which case IM-MS can separate the isomeric forms. Much of our IM-MS research aims emphasize development of new and better strategies for IM-MS, i.e., increasing the separation resolving power, increasing overall instrument sensitivity, and enhancing ion structure determinations. For example, we recently showed that the IM-MS resolution performed at low temperatures (90 deg. K) is ~ 4 times greater than that performed at 300 deg K, which is in excellent agreement with theory. We are also developing instrumentation that will allow dimensions for structure interrogation of mobility-separated ions. For example, we are developing capabilities for using fragmentation techniques such as CID, SID, photodissociation and ion-molecule reaction chemistry (hydrogen/deuterium exchange (HDX)) to further probe the structure of the IM separated ions. These enhanced instrument capabilities will impact our research in the area of petroleomics, plant and microorganism lipidomics, and imaging MS.

New Proton-Ionizable, Calixarene-Based Ligands for Selective Metal Ion Separations

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Our research program in the design and synthesis of new proton-ionizable, calix[4]arene-based ligands and their evaluation and application in metal ion separation processes continues. The calix[4]arene framework provides an unusually versatile scaffold for the construction of new metal ion complexing agents. In our work, attention is focused upon calix[4]arene ligands with two pendant acidic side arms. Metal ion extraction by such a ligand is accompanied by proton loss from the ligand in the organic phase to form an electroneutral complex. This avoids the necessity for concomitant extraction of an aqueous phase anion into the organic medium in a solvent extraction or liquid membrane transport process and thereby markedly enhances the propensity for metal ion transfer into the organic phase compared to non-ionizable analogues.

Metal ion extraction efficiency and selectivity for the di-ionizable calix[4]arenes are used to probe the influence of structural variation within the ligand upon the complexation process. Results are then utilized in the design of second-generation ligands with superior properties. Competitive solvent extractions from aqueous solutions into chloroform are conducted for the five alkali metal cations and for four alkaline earth metal cations. For lead(II) and mercury(II), single-species extractions are performed.

Novel Membranes for Carbon Dioxide Removal from Natural Gas Based on Thermally Rearranged Polymers

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Thermally rearranged (TR) polymers are a relatively new class of high-performance gas separation polymers that are rearranged from polyimides containing ortho-position functional groups. These polymers have unusually high combinations of permeability and selectivity and high chemical resistance. Both of these characteristics are desirable for gas separation membranes, but many of the fundamental parameters of the TR process are not currently understood. Research in 2010-2011 has focused on understanding the effect of polyimide precursor synthesis route and varying ortho-position functional group on the transport properties of TR polymers.

The polyimide precursor ortho-position functional group is lost during the thermal rearrangement process. This leaving group was varied and the gas transport properties were characterized. The polymer used in this experiment was HAB-6FDA (3,3’-dihydroxy-4,4’-diaminobiphenyl and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride). HAB-6FDA, when imidized by thermal techniques, has hydroxyl groups in the ortho-position which undergo thermal rearrangement when heated to the appropriate temperature. These hydroxyl groups can be modified by adding a dianhydride, which undergoes an esterification reaction with the hydroxyl group to give a desired ester in the ortho-position. In addition to the post-imidization modification, acetate groups can also be added as a byproduct of chemical imidization.

Polymers with acetate ortho-position groups show nearly identical transport properties despite being synthesized through thermal and chemical imidization. However, polymers with bulkier ortho-position groups yield higher gas permeabilities and lower selectivities than smaller ortho-position groups and transport properties are independent of synthesis route. These groups can be used to tune TR polymer transport properties and future work will explore additional ortho-position functional groups.

Theoretical and Experimental Study of Electrokinetic Accumulation and Separation

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During the current project period we have concerned ourselves with understanding how bipolar electrodes (BPEs) can be used for analyte enrichment, separation, and detection. Our approach has been to combine experiments carried out in our lab with high-level simulations provided by our collaborator, Professor Ulrich Tallarek (Philipps-Universität Marburg, Germany). These studies have resulted in a semi-quantitative understanding of the fundamental principles of bipolar electrochemistry. An important aspect of BPEs is that they do not require a direct external electrical connection. This means they are well-suited for both nanoscale electrochemistry applications, where it might be difficult to make such a connection, as well as for high-density electrode array applications, where it would be impractical to make thousands or millions of individual electrode connections. Our accomplishments during the past year including the following milestones.

- We reported concentration enrichment of analytes using a simple bipolar electrode arrangement, used simulations to elucidate the underlying principles of the method, and then designed and executed experiments to confirm the simulations. This method, which we now call bipolar electrode focusing (BEF), is probably the simplest method known for accessing enrichment factors of up to 500,000.
- We showed that BEF can be applied to mixtures of analytes, and that each analyte concentrates and separates in a unique location depending on its electrophoretic mobility.
- We described the first example of "two-dimensional" bipolar electrochemistry and elucidated its basic principles.
- We published an initial report showing that ion concentration polarization can be implemented using a bipolar electrode, rather than a nanochannel, to connect two microfluidic channels. This simplifies the methodology and expands its scope.
- We reported the first example of a faradaic electrochemical process powered by pressure-driven flow rather than an external power source. This discovery is based on the principle of the streaming potential.

Analytical Spectroscopy Methods for Liquid/Solid Interfaces

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Liquid/solid interfaces play a key role in numerous aspects of energy-related chemistry. Many steps in chemical analysis (separation, preconcentration, selective detection) involve adsorption or binding of target species to chemically-modified solid surfaces in contact with liquids. The transport of molecules and metal ions to interfaces and laterally, along interfacial planes, influences the rates of surface reactions, catalysis, and the efficiency of chemical separation processes. Electrically charged or polarized interfaces are important in the control of chemical separations and of interfacial binding events and in the kinetics of electron-transfer reactions involved in generation, storage, and transformation of energy.

To understand chemical structure and reaction kinetics at interfaces between liquids and solids, this research program is developing new spectroscopic imaging methods for the analysis of chemical structure and molecular dynamics at liquid/solid interfaces. In particular, confocal Raman microscopy is being applied to determining the chemical composition of interfacial species and their evolution in space and time within single porous particles. In the past year, this experiment has been adapted to solid-phase extraction into single, sub-picoliter particles, enabling rapid, ultra-trace level Raman scattering detection in small volume samples. We have produced a greater than 100,000-fold concentration increase of trace-level polycyclic aromatic hydrocarbons within a 10-minute contact time with the source phase solution. Detection limits are low ppb, which is remarkable for detection by unenhanced Raman scattering. Current efforts are being directed at reducing the volume of the collecting particle by 1000-fold, to less than a femtoliter; this will not compromise detection limits but will reduce the equilibration time to ~6 seconds.

The kinetics of molecular transport and binding to surfaces, including surface diffusion and adsorption and desorption rates, govern the efficiency of chromatographic retention, heterogeneous catalytic reaction rates, and the speed of solid-phase extraction, mentioned above. These dynamics are currently being characterized by single-molecule fluorescence imaging, both on flat surfaces and within porous particles. The trajectories of individual molecules are recorded in single-molecule movies, and fit to transport models that can include both continuous diffusion and hopping events. Results from the current funding period have provided the first observations of single-molecule trajectories of molecules within porous particles.

Finally, changes in interfacial molecular populations and chemical structure in response to applied electrical potentials are being characterized by surface-enhanced Raman scattering (SERS) and single-molecule imaging. Small potentials applied to conductive surfaces can be used to manipulate the structure and properties of the interface; changes in structure are apparent in the vibrational spectra of surface-bound species and include potential-dependent proton transfer reactions and monolayer self assembly. Changes in the interfacial populations of polyelectrolyte ions in the double-layer in response to changes in applied potential are monitored by fluorescence imaging, combined with counting of individual charged polymer molecules in the double layer.

The Hydrophobic Character of Nonsulfide Mineral Surfaces as Influenced by Double-Bond Reactions of Adsorb of Adsorbed Unsaturated Collector Species...

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Funding:	$135,000

The overall goal of this flotation chemistry research program is to provide a basis for improved flotation separation efficiency in nonsulfide mineral systems 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, as well as consideration of water film stability at mineral surfaces.

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. These results have been presented at professional society meetings and published in archival journals. In addition, AFM research continues with chlorite surface chemistry. The AFM measurements are being complemented with electrokinetic measurements, surface spectroscopy analysis, and molecular dynamics simulation.

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.

Finally, the issue of water film stability is being studied using sum frequency vibrational spectroscopy (SFVS). Initial experiments show that the SFVS spectra of water films at hydrophilic silica surfaces differ significantly from the spectra of water at a hydrophobic silica surface. The SFVS spectra indicate that a very ordered water structure exists in water films at the hydrophilic silica surface during contact with a bubble and that the extent of hydrogen bonding in the water film increases with an increase in contact pressure up to the point of rupture. The disposition of collector/frother molecules during bubble attachment and detachment is also being studied using sum frequency vibrational spectroscopy (SFVS). In the case of the dodecylamine/silica system, results indicate a significant increase in amine adsorption after bubble attachment which would correspond to an increase in adsorption density at the air/silica interface. Upon bubble detachment the amine is displaced from the silica surface. These results and future study should provide for a better understanding of the flotation process and the development of improved flotation technology.

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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Funding:	$80,000

Inelastic neutron scattering (INS) provides the ideal method to study the molecular vibrations of water adsorbed onto the surface of oxide nanoparticles as neutrons are highly sensitive to scattering by hydrogen atoms and much less sensitive to scattering from the metal oxides. 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. These studies provide an atomic scale understanding about the energetic and stabilities of nanoparticles. The research involves collaboration with Alexandra Navrotsky, Director of NEAT ORU & Thermochemistry Facility at U.C. Davis, and Brian Woodfield and Juliana Boerio-Goates, Department of Chemistry at Brigham Young University.

In addition to the INS projects completed on TiO_2, SnO_2, CoO and Co_3O_4 nanoparticles which have resulted in six publications, we have determined the thermodynamic properties of water confined on the surface of PdO nanoparticles. PdO-based nanoparticle systems have been extensively studied due to their interesting and varied chemical and physical properties. 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, Parker and Ross, 2011, JPCM, submitted). We also have two projects in progress:

(1) Alumina ($Al2O_3$) nanoparticle materials are of tremendous commercial importance and are employed in a broad range of applications including wastewater decontamination, catalysis supports, and in polymer composites for advanced engineering applications. Common to all applications in which nanoparticles play a key role is the importance of the structure, chemistry, and especially the water adsorbed on the nanoparticle surfaces. Our INS studies will allow us to determine the structure and thermodynamic properties of the water confined on the surface on alumina nanoparticles.

(2) Iron oxide nanoparticles including hematite, Fe_2O_3, and magnetite, Fe_3O_4, are an inherent part of the environment in which we live, occurring in abundance in biological, geological and technological settings. With INS spectra, we will not only be able to evaluate accurately 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 iron oxides at low temperature. For example, it is known that the Verwey transition in magnetite is particle-size dependent, but the effect that hydration has on this transition is not known. Neutron scattering provides the ideal method to explore both of these properties.

The results gathered in these seminal studies clearly demonstrate how INS experiments provide a powerful probe to explore the dynamics and thermodynamic properties of water adsorbed on the surface of oxide nanoparticles. Such data will be of great interest in the technological development of metal oxide nanoparticle systems.

Laser Material Interactions Relevant to Analytic Spectroscopy of Wide Band Gap Materials

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Funding:	$90,000

ATOMIC LIGHT EMISSION DURING ABLATION OF ZNO AT 193 NM

Luminescence from atomic zinc when ZnO is observed during 193 nm excimer laser exposure at fluences well below those required for optical breakdown. We attribute the dominance of triplet-triplet transitions to the radiative decay of a 3d10–4p 5s autoionizing state produced by two-photon absorption. In other systems, the high electron and ion densities produced by the decay of an autoionizing state would yield optical breakdown at relatively low fluences. However, the ionization rate associated with the 3d10–4p 5s excitation is relatively low due to quantum mechanical interference effects, and breakdown is not observed until the fluence approaches 2 J/cm^2. Imaging experiments show the evolution of the neutral zinc trajectories from simple thermal desorption, to Knudsen layer behavior, to adiabatic expansion as the fluence is increased. Our work with ZnO was performed in collaboration with Lynn Boatner, ONRL.

POSITIVE ION EMISSION FROM ZNO DURING 193 NM EXPOSURE AT LOW FLUENCES

Zn+ is observed from single crystal ZnO during 193-nm exposure at fluences far below those required to produce optical breakdown. At fluences near 40 mJ/cm^2, the emission decays exponentially with exposure time, consistent with the depletion of pre-existing defects. Much higher intensities are observed in the initial stages of exposure at fluences near 100 mJ/cm^2, but rapid second-order depletion soon follows. This behavior is consistent with the production of Zn vacancies and adsorbed Zn+ during the first several laser pulses. The resulting decay kinetics are consistent with the recombination of adsorbed Zn+ at surface vacancies proceeding in parallel with Zn+ emission. The production of zinc vacancies in the near surface bulk of these samples has been verified by positron annihilation spectroscopy, performed in collaboration with Mark Weber, WSU.

POSITIVE ION AND NEUTRAL EMISSION FROM ZNO DURING 193 NM EXPOSURE AT HIGHER FLUENCES

Parallel studies of particle emission at fluences above 300 mJ/cm^2 show sustained emission of neutral and ionic zinc atoms as well as other species. As the fluence increases, a slow component of Zn+ emission appears with kinetic energies consistent with the ionization of neutral zinc atoms. We attribute ionization to the nonradiative decay of the Zn I 3d10–4p 5s autoionizing state excited by two photon absorption described above. As noted above, we expect that the resulting ion intensities would be much higher if ionization were not hindered by quantum mechanical interference effects.

Modeling Carbon Dioxide Capture and Separation in Zeolitic Imidazolate Frameworks

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Students:	0 Postdoctoral Fellow(s), 2 Graduate(s), 1 Undergraduate(s)
Funding:	$40,000

The research objectives of the present work are to understand the microscopic origins of the properties of zeolitic imidazolate frameworks (ZIFs), nanoporous metal-organic framework (MOF) compounds consisting of Zn^{2+} cations and organic imidazolate linker groups. We are focusing primarily on those properties of relevance to CO_2 capture and flue gas separation, elucidating the microscopic interactions between CO_2 and the ZIF using quantitatively-accurate first-principles techniques, which further allow us to decompose this interaction into it constituent physical components (electrostatic, polarization, Pauli repulsion, dispersion, etc.)

We are utilizing symmetry adapted perturbation theory (SAPT) to construct force-fields tailored to study CO_2 adsorption in nanoporous ZIFs. Our approach utilizes the SAPT energy decomposition to generate physically-motivated force fields for the CO_2-CO_2, N_2-N_2, and CO_2-ZIF interaction, with explicit terms representing exchange, electrostatic, induction and dispersion interactions. Each of these terms is fit to the corresponding term in the SAPT energy decomposition, yielding a force field entirely free of empirical parameters. Due to the physical nature of their construction, these force fields are robust and transferable to environments for which they were not specifically parameterized. Furthermore, the explicit correspondence between force field terms and fundamental interaction types (dispersion, electrostatics, induction) allows for an analysis of the underlying physics controlling gas absorption that is not possible with the generic force fields that had been previously utilized to study these systems. As our force fields are free from empirical parameters, these results demonstrate the potential for computationally screening novel ZIFs for flue gas separation applications with near quantitative accuracy. Although we have focused specifically on the CO_2-ZIF system, we expect the general methodological approach, generating physically-motivated force fields via SAPT, to be widely applicable to a variety of complex systems ranging from gas adsorption to bio-molecular interactions.

We are also examining the possible role of common flue gas contaminants (water, NOx, SOx) with various MOFs, focusing specifically on those containing unsaturated metal centers. Here the under-coordinated metal strong binds a CO_2 molecule, leading to high uptake and thus excellent adsorption/separation properties. These same properties may also yield strong interactions with flue gas contaminants. We utilize quantum calculations to examine the binding strength of various contaminants with representative unsaturated MOFs, and employ simple statistical-mechanical models to estimate the implications of flue gas contaminants on the thermodynamics and dynamics of gas separation. We also consider the possible implications for such contaminants on framework stability.

DOE National Laboratories

Separations and Analyses (Chemical Analysis of Nanodomains)

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Students:	1 Postdoctoral Fellow(s), 6 Graduate(s), 0 Undergraduate(s)
Funding:	$600,000

The goals of this research are to develop novel instrumentation and methodologies for the analysis of phenomena that occur at nanometer length scales and picosecond time scales. We are focused on the ability to analyze phenomena on the molecular scale and at ambient laboratory conditions; our developed techniques will allow phenomena to be studied at the molecular scale under relevant conditions (i.e., without the use of vacuum or intrusive probes that can alter the properties being measured). We are applying these new instrumentation and methodologies to model systems of interest to the DOE mission. Fundamental insight can be gained with the high spatial and temporal resolution afforded by our developed methods including chemical catalysis in heterogeneous silica supported catalysts, the organization and dynamics of mixed model lipid bilayers and plant cell membranes, and heterogeneous enzyme catalyzed reactions.

The methods we are developing include (1) high resolution total internal reflection (TIR) Raman microspectroscopy and imaging; (2) sub-diffraction limited imaging, including differential interference contrast (DIC) microscopy, variable-angle evanescent-field (EFM) microscopy, and time-resolved stimulated emission depletion (STED) microscopy; and (3) novel single molecule spectroscopies.

Separations and Analyses (Mass Spectrometric Imaging of Plant Metabolites)

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Lee, Young-Jin, AMES LABORATORY
Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $195,000

Plants integrate biochemical machineries that are distributed among different cell-types and subcellular compartments to achieve net metabolic conversions. Techniques that can track intermediate metabolites as they move through a distributed metabolic network, and simultaneously become chemically interconverted are needed to directly demonstrate the nature of the network and its regulation. Our long-term objective is to develop mass spectrometric imaging techniques and determine the distribution of plant metabolites at the level of a single cell and subcellular compartments; mass spectrometry not only allows positive identification of the many plant metabolites but can also reveal the substrates and precursors involved in each metabolic pathway. These techniques are being developed in the context of understanding plant metabolic processes that are integral to highly efficient energy capture and storage, and are therefore at the core of DOE's mission.

Analogous to matrix-assisted laser desorption ionization (MALDI), we are developing methods that use a laser beam to interrogate, sequentially, micrometer areas of a plant by vaporizing the surface contents of the tissue into a mass spectrometer. Rastering of the laser beam over the tissue produces a laterally-resolved image of the various substances within different structures of the plant. Repeated vaporization at the same focused point of a plant structure will produce a depth profile of the components. Our research also includes generating ions directly from the plant tissue by designing novel additives as pseudo-matrixes. By minimizing sample preparation, compositional integrity and spatial resolution of the analysis will be guaranteed. Identification of the metabolites is aided by new strategies in ion formation, fragmentation, and high-resolution mass analysis. Spatial resolution will be pushed to the low micron regime by optimizing the optics and by increasing the detection efficiency.

Laser Materials Interactions (Ablation)

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Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
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; 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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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$850,000

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 in 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.

Improving Chemical Separations through Understanding of Weak Interactions

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Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $400,000

The goal of this research is to achieve a predictive understanding of the molecular-level interactions in solution that drive the affinity and selectivity between target ions and receptors in chemical separations. Theoretical and experimental efforts will be aimed toward understanding the specific contributions of solvation environment to selectivity in extractive separations. Determining local structure in solution will provide the experimental basis for new understanding of changes in entropy in solvation and binding; molecular-level modeling of solvation and binding interactions will strengthen predictive capabilities for anion extraction; and detailed investigations of the liquid-liquid interface will provide new insights into interfacial effects on extractive separations. To accomplish these specific aims we will take advantage of available and emerging capabilities in neutron scattering and computational sciences at ORNL. Success in this research will enhance the molecular-level predictability of extractive separations, extending the current capabilities from separate quantum mechanical considerations of individual ion-receptor interactions and structural determinations in ordered solids, to a bridging understanding of the important effects of solvent rearrangement on extractive separations. These new capabilities will contribute directly to DOE missions in energy production and utilization, environmental remediation, and to national and energy security.

PECASE Award Unraveling the Details of Ionic Liquid Mediated Biomass Fractionation

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Principal Investigator: Baker, Gary
Sr. Investigator(s):
Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $50,000

Pretreatment of biomass is essential for disrupting highly ordered and crystalline plant cell walls and for loosening lignin and hemicellulose conjugation to cellulose microfibrils. In particular, pretreatment facilitates enzyme accessibility and adsorption as well as producing less crystalline cellulose more suitable to downstream processes to produce bioethanol. However, the pretreatment step represents a considerable scientific challenge. This situation arises both from the complexity of biomass itself and the general recalcitrance of cellulose to conventional solvents, which limits its use and prevents economically viable conversion into value-added products. In the proposed work, our aim is to understand and control the fractionation of lignocellulosic biomass into its components. Initial emphasis will be placed on developing a molecular-level understanding of solvation of lignocellulose, dissolution, separation, and regeneration employing ionic liquids (ILs) as solvents, which have shown remarkable promise for cellulose processing. In addition to probing microcrystalline cellulose (e.g., Avicel) in benchmark dissolution studies, we will also investigate the selective lignin extraction from various sources, including wood flour and pristine switchgrass (Panicum virgatum). This research will begin to establish the molecular mechanism accounting for cellulose dissolution in IL solvents and promote the development of reliable, clean, and affordable energy from renewable sources.

Principles of Chemical Recognition and Transport in Extractive Separations

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Students:	3 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$1,170,000

The overarching goal of this program is 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.

Research in Advanced Chemical Measurements Technology

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$580,000

The objective of this program is to provide an understanding and control of the ultrafast energy flow in nanoparticles and their reactions and dynamics by imaging individual nanoparticles with chemical contrast and nano-scale spatial resolution. Chemical contrast is derived from the chemical heterogeneity of the sample and the molecular vibrations of interfacial molecular species. Our approach is linear and nonlinear optical spectroscopy as a means to probe important 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 environment. The scientific questions we wish to answer include:

(a) Can we monitor surface reactions of individual nanoparticles?

(b) What are the effects of metal nanoparticle size and morphology on their spectra and catalytic processes?

(c) Can we prepare unique nanoparticle structures by assembly of individual particles where the cluster creates extraordinarily large optical fields for surface enhanced techniques, such as Raman scattering, and for photocatalysis?

(d) Can we understand charge and energy transport within heterogeneous, polymeric nanostructures of photovoltaic interest using pump-probe spectroscopy and by mapping picosecond time-resolved fluorescence?

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 the 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.

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

The overarching goal of the research within this proposal is to advance the capacity of mass spectrometry (MS) to study and characterize the reactions and molecular products of redox transfer processes and to study and characterize with nanometer spatial resolution molecular constituents of surfaces under real world conditions. 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, battery electrodes, catalysis, biomass recalcitrance and productivity, and chemical sensor systems that are critical in the Department of Energy (DOE) energy research and national security missions. In the present proposal, there are two specific aims. The first specific aim of our work is to understand and implement the means to efficiently desorb (extract) and ionize surface species and then efficiently collect and transport at atmospheric pressure (AP) the ions created, with emphasis on approaches that utilize gas/liquid jet desorption, thermal desorption, or laser desorption to sample/ionize surface constituents. A portion of the research is focused on conceptualizing and characterizing new interface concepts for coupling electrochemistry and mass spectrometry with the second specific aim to understand and implement the means to overcome the compromise between an optimum solution/electrolyte composition for electrochemistry and that needed for MS to improve the utility of online electrochemistry/mass spectrometry. The knowledge gained from this research will enable existing mass spectrometric analysis and characterization methods to be enhanced and ultimately transcended. As such, new fundamental information and research capabilities from mass spectrometry science will emerge that can address new problems relevant to many DOE missions and the general scientific community.

Change Transfer, Transport, and Reactivity in Complex Molecular Environments: Theoretical Studies for the Hydrogen Fuel Initiative

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$350,000

This theory program aims to develop, implement, and apply new theoretical and computational methods that will enable a fundamental understanding of charge transfer and transport that are basic to critical processes in the Hydrogen Fuel Initiative. Selective transport of protons and ions through membranes is central to the operation of fuel cells. The theoretical description of such charge transport processes in systems is challenging because of the diversity of transport mechanisms, their dependence on local structure in complex molecular environments, and their coupling with chemical reactions. The development of new theoretical and computational methods to improve the molecular-level understanding and control of these processes is essential for the rational design of the materials needed for a viable hydrogen economy. The program is fundamental in nature and supports one of the high priority research directions of the Hydrogen Fuel Initiative.

Chemical Analysis

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Sr. Investigator(s):	Futrell, Jean, PACIFIC NORTHWEST NATIONAL LABORATORY Zelenyuk, Alla, PACIFIC NORTHWEST NATIONAL LABORATORY
Students:	2 Postdoctoral Fellow(s), 1 Graduate(s), 1 Undergraduate(s)
Funding:	$730,000

The goal of our research is development and application of advanced mass spectrometric methods to challenging analytical chemistry problems of interest to DOE. In particular, we develop unique instrumentation and use these research tools to investigate fundamentals of mass spectrometry of complex molecules, to characterize the fundamental properties of individual nanoparticles, and investigate the processes that govern their chemistry and microphysics on the nanoscale. These tools also provide the ability to measure simultaneously with extreme sensitivity and precision changes in size, shape, density, fractal dimension, hygroscopisity, and composition in controlled laboratory environments. Our experiments focus on achieving a broad understanding of the chemical and physical properties of aerosols over their relevant life cycle, employing advanced experimental methods to investigate the kinetics of these processes. The range of relevant experiments encompasses laboratory investigations of particles shown by field studies utilizing single particle mass spectrometers and particle collection to identify the most relevant conditions. Very large multidimensional data sets are processed using novel approaches to data mining and visualization. Complex ion reaction dynamics are investigated using a novel multi-stage tandem mass spectrometer that collides energy and mass selected ions on a surface within a superconducting magnet where products recoiling from specially prepared semiconductor surfaces are analyzed by Fourier Transform mass spectrometry. Surface-induced dissociation on tailored semiconductor surfaces advances both our fundamental knowledge base and techniques for analysis of complex molecules. For low-energy ion-surface collisions, the major process competing with surface-induced dissociation (SID) is ion loss by neutralization or soft-landing on the surface. A new apparatus that deposits relatively intense ion beams on surfaces and a novel Surface Ionization Mass Spectrometer (SIMS) gun has been added to our tandem SID-FTMS for real-time analysis of surface composition. Soft landing, adsorption of intact ions on the surface, ion reactions with the surface and kinetic energy driven bond formation are new areas of investigation.

Mass Spectrometry for Operando Catalysis Research

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$50,000

Unique capabilities offered by the atmospheric sampling techniques open up a wide range of applications relevant to many scientific fields. In particular, recent development of atmospheric pressure surface ionization techniques such as desorption electrospray ionization (DESI) or direct analysis in real time (DART) and other related methods 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. If successful, this will result in a breakthrough class and new capability for studying the catalysis of thermal and photon-driven heterogeneous reaction.

Solar Photochemistry

Institutions Receiving Grants

Magnetic Resonance and Optical Spectroscopic Studies of Carotenoids

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Dixon, David, ALABAMA, UNIVERSITY OF
Molnar, Peter, PECS - HUNGARY, UNIVERSITY OF
Students: 2 Postdoctoral Fellow(s), 2 Graduate(s), 2 Undergraduate(s)
Funding: $145,000

The objective of this study is to determine how the host lattice 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. Carotenoid radical cations have been identified in photosystem II (PS II) due to the role of carotenoids as intermediate electron carriers in the reduction of P680+ by chlorophyll (Chlz) and Cyt b559 to protect PSII against uncontrolled oxidative reactions of the oxidizing P680+; confirmed by genetic modification, (Bautista, et al., J. Biol. Chemistry 280, 38839 (2005)), supported by EPR (Lakshmi, et al., JACS, 125, 50005 (2003), and by the X-ray structure of PS II (Vasileu, FEBS, 543, 159 (2003)). Carotenoid radical cations also serve to dissipate excess energy and thus protect the plant against sunlight that is not needed. For instance, deactivation of 1Chl* during excess light occurs by excitation transfer to a chlorophyll-zeaxanthin heterodimer, followed by ultrafast Zea+• formation (Science, 307, 433 (2005)). Studies have shown that water soluble complexes of carotenoids exhibit a significant increase in photostability and give rise to more efficient TiO_2 photocatalyst. Free radical formation has been studied in novel carotenoid metal ion complexes of astaxanthin in an attempt to understand its photoprotection and antioxidant properties.

Supramolecular Structures for Photochemical Energy Conversion

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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.

Electronically Wired Semiconductor Nanoparticles: Toward Vectoral Electron Transport in Hybrid Materials

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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.

In this new work we will pursue the following specific goals:

(1) Develop new ligand-capped CdSe (and related II-VI semiconductor nanocrystals [SC-NCs]) rods, and related asymmetric nanocrystals, providing for selective and asymmetric addition of catalytic metallic and oxide (e.g. cobalt oxide) catalytic sites, with unprecedented control over the placement, electronic coupling, and catalytic activity of these sites on the SC-NC. These modifications to NC materials will retain the electroactive capping ligands we developed in the first phases of this project;

(2) Extend our recently developed protocols for the study of monolayer-supported SC-NCs, using high vacuum UV -photoemission spectroscopies (UPS), for characterization of EVB and local vacuum level changes as a function of surface coverage on the nanomaterial – we will specifically probe Iigand/NC, NC/NC and NC/metal or metal oxide interactions which change the frontier orbital energies of the NC in ways that are expected to impact on solution and condensed phase charge transfer processes;

(3) Extend our recently developed protocols for the spectroelectrochemical study of monolayer supported SC-NCs on electroactive waveguide substrates. As with our UPS studies, these waveguide-based protocols allow us to study NC-NC interactions which influence ECB, EVB as a function of NC-NC spacing on the surface, the presence of dipolar ligands, and the introduction of asymmetric nanorods, and nanorods modified with catalytic sites. These studies are coupled with unique spectroelectrochemical characterization of rates of photoelectrochemically-induced ET to the surface-confined NC, and to solution probe molecules.

(4) Extend our recently developed protocols for conductive tip atomic force microscopy (C-AFM) characterization of the J/V properties of heterogeneous electrodes to the characterization of single surface-tethered NCs, and to small clusters of interacting NCs.

(5) Develop the first prototypes of membrane encapsulated ensembles of these asymmetric, modified SC-NCs, using reflectance spectroscopies to probe the energetic of ET processes in these membrane-supported nanomaterials, and the first demonstration of proton pumping in response to photoelectrochemical events on either side of the membrane.

Development of Inexpensive, Abundant Semiconductors for Solar Energy Conversion: Photoelectrochemistry of Zn_3P_2, FeS_2, and WS_2 for the Production of S

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Low cost, earth-abundant light absorbers are of great interest for use in terrestrial photovoltaics and in artificial photosynthesis. Currently, silicon is the only commercially available solar absorber material that has the potential to deliver terawatts of power. The lack of inexpensive solar absorbers remains a bottleneck for development of next generation photovoltaics and tandem solar water-splitting cells. Zinc phosphide (Zn_3P_2) and cuprous oxide (Cu_2O) showed promising energy-conversion properties in the early research in the 1980s. However, the highest efficiencies reported from Zn_3P2-based and Cu_2O-based solar conversion device were limited to 6% and 4%, respectively. Lack of knowledge of surface and interface properties of the two materials prevented their applications in photovoltaics and photoelectrochemical cells, and research all but ceased in the mid 1980s. Our work aims to leverage modern analytical techniques and understanding of semiconductor physics and chemistry in order to produce Cu_2O and Zn_3P_2 solar absorber materials with unprecedented energy-conversion properties.

Zn_3P_2 is a semiconductor material with light absorption and electronic properties that make it appear promising for solar energy conversion applications. However, previous research has been heavily limited by the inability to control the chemistry related to synthesizing high quality Zn_3P_2 crystals as well as controlling the critical surface and interfacial properties that enable high efficiency solar devices. We have developed synthesis and surface chemical treatments that have been demonstrated by photoluminescence studies to significantly decrease the prevalence of parasitic surface defects. Thus, our work on Zn_3P_2 has allowed this material to come closer to reaching its full potential as a solar absorber material.

The theoretical efficiency of a Cu_2O-based solar conversion device under AM 1.5 illumination is on the order of 20%. However, the highest efficiency reported for a photovoltaic incorporating Cu_2O to date is only 4%. The major challenge for formation of highly efficient Cu_2O cells has been, similar to Zn_3P_2, sufficient control over surface and interface chemistry that avoids formation of parasitic chemical species. We have overcome this difficulty by using a unique configuration, a semiconductor/liquid junction, which is able to circumvent the problems with deleterious surface and interface reactions. In this configuration, we have demonstrated Cu_2O-based solar cells that generate large photovoltages in sunlight. This key improvement demonstrates that high efficiency solid-state junctions may be realized with rigorous control of the surface chemistry and surface passivation of Cu_2O absorbers.

Sunlight-Driven Hydrogen Formation by Membrane-Supported Photoelectrochemical Water Splitting

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We are developing an artificial photosynthetic system that will only utilize sunlight and water as the inputs and will produce hydrogen and oxygen as the outputs. We are taking a modular, parallel development approach in which the three distinct primary components-the photoanode, the photocathode, and the product-separating but ion-conducting membrane-are fabricated and optimized separately before assembly into a complete water-splitting system. The design principles incorporate two separate, photosensitive semiconductor/liquid junctions that will collectively generate the 1.7-1.9 V at open circuit necessary to support both the oxidation of H_3O (or OH-) and the reduction of H^+ (or H_3O). The photoanode and photocathode will consist of rod-like semiconductor components, with attached heterogeneous multi-electron transfer catalysts, which are needed to drive the oxidation or reduction reactions at low overpotentials. The high aspect-ratio semiconductor rod electrode architecture allows for the use of low cost, earth abundant materials without sacrificing energy conversion efficiency due to the orthogonalization of light absorption and charge-carrier collection. Additionally, the high surface-area design of the rod-based semiconductor array electrode inherently lowers the flux of charge carriers over the rod array surface relative to the projected geometric surface of the photoelectrode, thus lowering the photocurrent density at the solid/liquid junction and thereby relaxing the demands on the activity (and cost) of any electrocatalysts. A flexible composite polymer film will allow for electron and ion conduction between the photoanode and photocathode while simultaneously preventing mixing of the gaseous products. Separate polymeric materials will be used to make electrical contact between the anode and cathode, and also to provide structural support. Interspersed patches of an ion conducting polymer will maintain charge balance between the two half-cells. The modularity of the system design approach allows each piece to be independently modified, tested, and improved, as future advances in semiconductor, polymeric, and catalytic materials are made. Hence, this work will demonstrate a feasible and functional prototype and blueprint for an artificial photosynthetic system, composed of only inexpensive, earth-abundant materials, that is simultaneously efficient, durable, manufacturably scalable, and readily upgradeable.

Membrane-Organized Chemical Photoredox Systems

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The ruthenium "blue dimer" is the first well-defined molecular catalysts able to sustainably catalyze water oxidation at low potentials. However, it has been subject to a number of spectroscopic and computational studies, and the mechanism of water oxidation remains unsolved. Of particular interest is the mostly highly oxidized state of the dimer present prior to O – O bond formation. This state is termed as the {5, 5} state. We are performing the advanced EPR studies on the g ˜ 2 signal that was previously assigned to {5, 5} species. Continuous wave (CW) EPR is being used to characterize the large ruthenium hyperfine coupling. Additionally, electron spin echo envelope modulation (ESEEM) and Hyperfine Sublevel Correlation spectroscopy (HYSCORE) experiments are used to probe the 14N hyperfine coupling that originates from the bipyridine ligands. Electron-nuclear double resonance (ENDOR) is also implemented to monitor chemically exchangeable protons. Our studies are probing the S = 1/2 state of the {5, 5} and to test for evidence of an alternative intermediate with an odd overall electron count (per dimer). It is possible that the Ru ions in the {5, 5} state are not true RuV species. One suggestion based on previously reported DFT proposes that the bipyridine ligands are being dearomatized via a covalent hydration mechanism, allowing for the Ru ions to be < V oxidation state.

Exciton Transport and Charge Separation in Quantum Dot Arrays

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Several aspects of the spectroscopy and dynamics of semiconductor nanocrystals have been studied. We have studied the dynamics of biexcitons in CdSe nanoparticles are examined as a function of the magnitudes of internal electric fields. The results show that the presence of strong internal fields results in rapid Auger recombination. The strengths of the electric fields and hence the Auger recombination rates are controlled in several different ways: specifically, by varying the dielectric constant of the surrounding solvent, by changing the particle surface stoichiometry and hence the magnitude of surface charges, and by inducing a piezoelectric field through the deposition of a lattice-mismatched shell material. In other studies, highly luminescent type-II CdTe/CdSe core/shell and core/tetrapod heterostructure quantum dots (QDs) have been synthesized. These morphologies exhibit very different spectroscopic properties as a result of lattice mismatch effects. The lattice mismatch results in a calculated core pressure of about 3.4 GPa for the particles with the thickest shells. This pressure causes a change in the CdTe conduction band energy of about 0.3 eV and a change in the lattice parameter of 2.6%. The change in the lattice parameter is also seen in HRTEM and XRD data. Annealing of these particles results in core-shell interdiffusion, producing an alloyed region at the core-shell interface, further shifting the spectrum to the red. These spectra may be quantitatively understood in terms of calculated radial composition profiles and the known elastic and optical band-bowing parameters of CdTe-CdSe alloys.

In a related project, transient absorption spectroscopy has been used to study the rates of electron transfer (ET) from CdSe and CdSe/ZnS core/shell nanorods to adsorbed methyl viologen, MV2+. The nanorods are excited with 387 nm light, producing electrons 7700 cm-1 above the conduction band edge. Kinetics are measured in particles without adsorbed MV2+, giving electron cooling and electron-hole recombination times. The kinetics obtained with and without adsorbed MV2+ are compared to infer the ET rates. The results indicate that electron cooling occurs on the 0.7 to 1.8 ps timescale, with the fastest cooling occurring from the highest energy states. Hot electron transfer from the highest energy levels competes with electron cooling, occurring on the 0.5 ps timescale. Bare particle (relaxed) electron transfer occurs on the timescale of less than or about 4 ps, which is faster than biexciton Auger recombination which occurs on the 50 ps timescale.

Fundamental Studies of Energy- and Hole/Electron-Transfer in Hydroporphyrin Architectures

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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.

(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.

Nanoscaled Components for Improved Efficiency in a Multipanel Photocatalytic Water-Splitting Device

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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 need contribute only a fraction of the overall potential required for water splitting, thus permitting device engineering to maximized efficiently without regard to electric potential. In our experiments, we found that Ti plates, vacuum and water have shown very important influences on the photocatalytic properties of TiO_2 films.

The multipanel cells were constructed from a quartz tube (15mm in diameter) cut at 4-cm intervals at 45° angles. Each segment had a filling port through which electrolyte could be added. The electrodes were glued between the segments with epoxy with all of the platinum sides facing in the same direction. Different from our previous design, Nafion films were mounted. The Nafion films separated two aqueous solutions. The TiO_2 sides were filled with an aqueous NaOH solution (1M) and Pt side with an aqueous H_2SO_4 solution (0.5M) in order to provide a small chemical bias assisting electron transfer from the TiO_2 surface layer to the Pt side during irradiation.

We have successfully constructed a multi-cell assembly and demonstrated separated generation of hydrogen and oxygen. However, reproducibility has been an issue with preparation of the metal oxide faces, an area that we are actively exploring as this remains a central and critical issue for tuning other parameters in the assembly.

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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One of the major challenges of the 21st Century is to develop new energy sources of sufficient capacity to meet steeply growing demand and whose use is not detrimental to the environment. The conversion of solar radiation to a benign chemical fuel would meet these criteria. This research 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 for artificial photosynthesis, because these compounds possess the highly reducing excited states needed to activate inert solar-fuel substrates and the proton-coupled electron-transfer (PCET) chemistry that could allow them to function without conventional sacrificial donors. These attributes mesh with the key needs for advancing the artificial-photosynthetic conversion of carbon dioxide to solar fuels. The project has three major objectives. First, it aims to understand the excited-state electron-transfer mechanisms and rates of highly reducing MCR–porphyrin dyads via systematic variation of their electron-transfer driving forces, donor–acceptor electronic coupling, and the positioning of secondary donors that provide a spatial electron-transfer gradient. These results will be interpreted within the framework of fundamental electron-transfer theories and provide insights that will enable the design of functional assemblies that possess the charge-separation lifetimes necessary to drive catalytic carbon dioxide reduction. Second, the research project aims to develop for MCR compounds a catalytic PCET cycle that provides electrons for photochemical carbon dioxide reduction without conventional sacrificial donors. These cycles are based on a novel scheme in which metal–hydride catalysts mediate the transfer of hydrogen atoms to the oxidized reaction center, ultimately providing the electrons consumed in solar fuel production from the activation of dihydrogen or of organic dehydrogenation substrates. Third, the research aims to design and study MCR–antenna–catalyst assemblies for the photochemical one- and two-electron reduction of carbon dioxide. The one-electron reduction assemblies, based on palladium-porphyrin–MCR dyads, provide simple test beds with which the integration of the fundamental concepts developed in Objectives one and two can be explored.

The results of these studies will be applied to more complex porphyrin–MCR assemblies that contain efficient rhenium catalysts; these will photochemically reduce carbon dioxide to carbon monoxide, which is a valuable fuel feedstock. Completion of these three objectives will result in catalytic artificial-photosynthetic cycles for the generation of solar fuels. 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. The molecular assemblies we are studying allow these questions to be studied and provide prototypes for further development.

Transition Metal Polypyridine Complexes: Studies of Mediation in Dye-Sensitized Solar Cells and Charge Separation in Molecular Assemblies

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Bisphenanthrolinecopper(I) is a visible-light-absorbing chromophore that affords an earth-abundant alternative to ruthenium complexes for the fabrication and study of Donor-Chromophore-Acceptor assemblies (D-C-A) that affect light-induced, multistep charge separation. Copper(I) coordination chemistry presents a number of different synthetic challenges to those presented by ruthenium(II). Moreover, its photophysics and excited-state redox chemistry differ from related ruthenium complexes in important ways. First, Cu(I) complexes are labile; thus, thermodynamics (rather than kinetics) must be exploited to obtain the desired complexes in solution. Second, the MLCT excited state bisphenanthrolinecopper(I) is a powerful reductant but a weak oxidant. Furthermore, the bisphenanthrolinecopper(II) resulting from oxidative quenching of the MLCT state is only a modest oxidant. As a consequence of these facts, different strategies are required to develop D-C-A assemblies that undergo efficient light-induced Charge Separated State (CSS) formation. Nonetheless, much of what we have learned in our prior studies with assemblies based on ruthenium chromophores has been invaluable in designing copper based systems for study.

We have succeeded in synthesizing D-C-A triads and C-A diads and conducted preliminary nanosecond transient absorption studies on these, both in the presence and absence of applied magnetic fields. These studies have exposed a number of interesting features of the systems. First, unlike the ruthenium analogs, the C-A diads yield a moderately long-lived (10s of nanoseconds) charge-transfer state (CT) where the Cu is oxidized and the viologen acceptor is reduced. The CT state is formed with good quantum yield but less than unity. We have also prepared a copper-based D-C-A triad incorporating the identical acceptor-containing ligand as in the diad but also incorporating an appropriate electron donor. This assembly undergoes efficient multi-step CSS formation where the acceptor is first reduced (just as in the CT state of the C-A diad) but then the hole is subsequently transferred from the Cu(II) to the donor. Again, the QE for this process is large but probably not unity. The rate of recombination of the CSS is highly magnetic and field-dependent. In fields of only a few mT, the decay of the CSS becomes distinctly biexponential with a fast component which appears to be approximately field-independent, and a slow component whose rate decreases with increasing field up to fields of about 1.0 T. This behavior is qualitatively similar to what is observed for analogous Ru-based systems. There are, however, interesting differences from the Ru case: (1) the lifetime of the slow component is ca. ×100 slower than the fast component (60 ns vs. 6000 ns) and (2) the QE for CSS appears to be field dependent at low fields. We currently are working to develop a quantitative understanding of these systems, especially the intriguing spin chemistry.

In the second aspect of this study we are investigating high potential trisbipyridinecobalt(II/III) mediators for Dye Sensitized Solar Cell (DSSC) applications. One of the many advantages of trisbipyridinecobalt(II/III) complexes as mediators in DSSCs is the fact that the redox potential can be tuned by changing substituents on the bipyridine ligand. With strong electron-withdrawing substituents such as carboxyamides, the E1/2 can be shifted by ca. 450 mV to higher potential relative to alkyl substituents in the same position. We have synthesized a series of cobalt complexes of bipyridine ligands substituted in the 4 and 4'-positions with secondary and tertiary amides. The alkyl substituents on the amide nitrogens differ in their steric bulk and degree of branching, but all have very similar redox potentials. Generally speaking these complexes result in significantly higher open circuit voltages for DSSC's dyed with the most common dye (N_3), but they also have lower short circuit currents relative to what is observed with trisDTBcobalt(II/III) as mediator (DTB = 4,4'-di-t-butyl-2,2'-bipyridine). We are currently assessing the reasons for the lower short circuit currents. The three most likely origins are: (1) more rapid recombination with the photoinjected electrons, (2) slow mass transport of the oxidized form of the mediator, or (3) slow regeneration of the reduced dye, or a combination of these factors.

We anticipate that mass transport issues with these complexes will be at least as significant as with trisDTBcobalt(II/III) given that all of the amide substituents are larger than t-butyl. There are several approaches to minimize the effect of mediator mass transport in these systems; however, in many instances they also impact other parameters that affect cell efficiency. There is evidence in the literature that atomic layer deposition (ALD) of materials such as alumina on the mesoporous photoanode improves cell performance, at least with cobalt-based mediators that have less positive potentials than those described above. We are in the process of studying the effects of ALD modification on DSSCs mediated with high-potential complexes. The expectation is that with an alumina tunneling barrier high-potential cobalt complexes with smaller substituents (than those above) may function well as mediators and have fewer issues with slow mass transport.

Study of Multiple Exciton Generation with New Multi-Dimensional Spectroscopies

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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. There are several obstacles facing the development of high efficiency third generation photovoltaics. One approach involves generation of multiple electron-hole pairs from a single photon. Recent femtosecond measurements of excess probe transmission at the band gap provide evidence for multiple electron-hole pair generation in semiconductor quantum dots, but there is controversy over the yield. The mechanism has been attributed to either impact ionization, direct carrier multiplication, or multiple exciton generation in various theories. As the principles and practice of making electrical contacts between quantum dots and electrical contacts are not fully developed, there is a pressing need for non-contact measurements of the material parameters involved in carrier multiplication. The effort proposed here 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.

The quantum mechanical change in the electronic state needed to generate multiple electron-hole pairs from a single pair requires both coupling and dephasing. Coupling, by itself, would cause population to oscillate back and forth between the coupled electronic states; dephasing stops the oscillations before they can proceed back to the starting state. 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, we plan to measure the dynamics of "hot" states with energies near the electron-hole pair multiplication threshold. Concurrently, we plan to directly characterize multiple exciton states, the couplings between single-excitons in a bi-exciton, and the dephasing dynamics of bi-excitons. All existing multidimensional optical and NMR spectroscopies probe the interactions between states with the same number of excitons. Provided that their dephasing is not dominated by unexpectedly fast population decay, a main thrust of the project will be to develop a new type of 2D spectroscopy to measure the coupling and dephasing between states with different numbers of excitons via multidimensional spectroscopy. The new approach envisioned involves direct measurement of the multi-exciton to single-exciton coupling via harmonic generation or the associated downconversion frequency mixing. Such novel spectroscopic approaches hold great promise as selective probes of the coupling needed for multiple-exciton generation. We anticipate that it will be quite important to quantify the role of both dephasing mechanisms in a variety of quantum confined materials. By the end of the project, we aim to develop sufficient mechanistic understanding of the process in a variety of semi-conducting quantum dots that its potential for third generation photovoltaics can be properly evaluated.

Graphene Charge Transfer and Photochemical Reactions

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This project focuses on the special electronic and optical properties of graphene. 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.

We have explored the question of possible surface enhanced Raman spectroscopy from charge transfer on graphene substrates. We observed strong hole doping of graphene by adsorbed halogens as indicated by the shift of the graphene G Raman band. In the case of iodine adsorption, we also observed the anionic species made by hole doping. At low frequency in the Raman spectrum, we saw quite intense lines from I3- and I5- species. The integrated intensity ratio of iodine anion to graphene G peak is about 120. We calculate this intense signal comes from only 3 % surface coverage.

Normally Raman spectra are too weak to allow detection of a monolayer. We have recently shown through accurate Fresnel calculations that a multilayer graphene film acts internally as a modest optical cavity for both laser and Raman light; for example G band Raman light generated inside graphene has a 36% back reflection probability at the graphene:air interface for normal incidence. An additional reason we can detect Raman signals from adsorbed species with high sensitivity is that the graphene quenches any interfering luminescence. On the graphene surface the iodine anions show a strong intramolecular resonance Raman effect from laser excitation directly into their excited states. Any luminescence from the excited state is quenched by energy transfer to graphene. Note also we find no evidence for either a field enhancement or chemical type of surface enhanced Raman effect (SERS).

Theoretical Studies of Photoactive Molecular Systems: Electron Transfer, Energy Transport, and Optical Spectroscopy

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Funding:	$180,000

We have been developing methods for studying complex systems using quantum chemical calculations based on density functional theory. By using a series of localized orbital corrections (LOCs), we have been able to dramatically improve a wide range of properties, including bond energies, atomization energies, ionization potentials, electron affinities, redox potentials, transition state barriers, and spin splittings and redox potentials in transition metals. Average errors for organic systems are ~1 kcal/mole and average errors for transition metal containing systems are 2-3 kcal/mole. We have also been applying DFT methods to systems of interest to the solar photochemistry program. We have performed a complete analysis of the catalytic cycle of a Ru-containing catalyst studied by Meyer and coworkers which is capable of performing water splitting and oxygen evolution. We achieve excellent agreement with experimental data for this system for barrier heights of the rate determining steps and hence for kinetics, in contrast with other results reported in the literature. Secondly, we have built a model for ambipolar diffusion in TiO_2 by injected electrons using large scale cluster DFT calculations involving ~350 atoms in the cluster. These calculations model the barrier for moving an electron in the TiO_2 from one site to another, assuming an ambipolar diffusion model in which an ion (we use Li^+ as is the case in the actual experimental system) moves with the electron and stabilizes the trapping state of the electron. The barrier to hopping that we obtain is compatible with hopping barriers estimated by Frank and coworkers based on experimental measurements of electron diffusion as a function of temperature and concentration.

Organic, Nanoscale, and Self-Assembled Structures Relevant to Solar Energy Conversion

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Understanding the molecular-level principles by which complex chemical systems carry out photochemical charge separation, transport, and storage will impact the design of practical solar energy conversion and storage devices. Towards this goal, this program focuses on (1) delineating new compositions of matter relevant to solar energy conversion; (2) elucidating factors that control charge transfer, charge migration, photoconductivity, and exciton diffusion dynamics in assemblies relevant to light-driven energy transduction; (3) probing the extent of electronic coupling between conjugated organic materials and nanoscale structures in both ground and excited states; and (4) engineering high quantum yield electron-hole pair production from initially prepared excitonic states in compositions that feature both molecular and nanoscale electrooptically active components.

Conjugated Polymers and Polyelectrolytes in Solar Photoconversion

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This research program is focused on fundamental investigation of the photophysical properties of conjugated polyelectrolytes (CPEs) and donor-acceptor (D-A) conjugated polymers. The objective of the program is to provide insight concerning the relationship between conjugated polyelectrolyte structure and the effect of donor-acceptor interactions on fundamental properties such as singlet and triplet exciton structure, exciton transport dynamics, amplified quenching, and charge separation arising from donor-acceptor interactions.

In one line of investigation during the past year we have synthesized and used photophysical methods to study energy transport in conjugated polyelectrolyte dendrimers (CPDs) and conjugated polyelectrolyte oligomers (CPOs). First, second and third generation CPDs have been studied and steady-state spectroscopy reveals that energy transfer occurs with very high efficiency within the structures, from high energy chromophores in the periphery to a low energy chromophore that is in the dendrimer core. The spectroscopic results also indicate that the tendency of the CPDs to aggregate in aqueous solution increases with dendrimer size; however, fluorescence correlation spectroscopy and dynamic light scattering reveal that the aggregates are relatively small, suggesting the formation of dimers or trimers. Fluorescence upconversion spectroscopy results conclude that intradendrimer energy transfer occurs on a very fast time scale, with average time constants ranging from 1.5 - 3.5 ps, increasing with dendrimer generation number. Linear CPOs of precise length have been synthesized via an iterative sequence, affording molecules with 5, 7 and 9 repeat units, with overall charge of -12 (5), -16 (7) and -20 (9). Due to the high charge density, the CPOs do not aggregate in aqueous solution, and fluorescence studies reveal very efficient quenching by oppositely charged ions with Stern-Volmer constants as high as 107 M-1.

A second line of study has examined the synthesis of donor-acceptor conjugated oligomers that are functionalized with a single anionic carboxylate unit for anchoring to metal oxide surfaces. This work has led to the development of the N-alkylated benzotriazole unit as an acceptor moiety in a pi-conjugated system. A series of three donor-acceptor-donor type oligomers have been prepared, in which the core acceptor is the benzotriazole unit and the donors are thiophene segments of varying length. Preliminary studies show that the anionic carboxylate forms of these oligomers can be adsorbed to the surface of nanostructured TiO_2 and the systems undergo rapid charge injection into the metal-oxide following visible light excitation. Ongoing work is aimed at developing Gringard metathesis chemistry to prepare block polymers in which a core benzotriazole acceptor unit is flanked by two regio-regular poly(alkylthiophene) segments. The resulting donor-acceptor-donor polymers will be adsorbed to metal-oxide surfaces for photophysical and photoelectrochemical investigation.

The Design of a Photocatalyst for the Decomposition of Water into its Elements

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The project involves the design, synthesis, and study of transition metal catalysts that use the energy inherent in the photoexcited 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. With the discovery that mononuclear catalysts react by a first order pathway, more attention is being given to a mechanism involving the attack of H_2O on a Ru=O species. We are examining complexes of the type [Ru(tpy)(bpy)X]+ (bpy = 2,2'-bipyridine; tpy = 2,2';6,2''-terpyridine; X = halogen, H_2O) to determine if initial displacement of halide is mandatory. A family of catalysts having an equatorial tetradentate ligand is being studied to obtain further structural evidence for a possible 7-coordinate intermediate. In this regard, the importance of strain in the first coordination sphere of the metal is being assessed as a factor in expanding this sphere to 7-coordinate. The 1,8-naphthyridyl, and t-butyl group can promote enhanced reactivity and these subtle features are being investigated in efforts to “tune” the catalyst. A still-active catalyst will be recovered and analyzed as a probe of mechanism and we will immobilize a catalyst on a surface such as TiO_2 or diamond and analyze reactivity. Dinuclear catalysts developed in the previous cycle of funding are being investigated to determine the possible advantage of multiple metal centers in managing access to higher oxidation states. A chromophore-catalyst dyad has been prepared that allows for activation of the catalyst by light and this exciting advance is being studied carefully. Together with Etsuko Fujita at BNL, bidentate and tridentate ligands containing the 4-azaacridine moiety are being investigated wherein the uncomplexed nitrogen on the central ring can mediate the transfer and ultimately the photoreduction of protons through an NADH-type intermediate. Overall a strongly synthesis-driven approach is being used to develop and study new and improved photocatalysts for water decomposition

Electron Transfer Dynamics in Efficient Molecular Solar Cells

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Our DOE-supported research has focused on the mechanisms for interfacial charge transfer at nanocrystalline TiO_2 interfaces. Our approach has been to characterize novel molecular and supramolecular sensitizers, based on $(d\pi)^6$ coordination compounds of our own design, with steady state and time resolved spectroscopic and electrochemical techniques. The proposed research described herein addresses the overall DOE scientific mission by advancing two interrelated frontiers in solar energy research: (1) surface electric fields that drive ion motion and influence energetics at semiconductor interfaces and (2) light driven bond-breaking and bond-making reactions that involve iodine-iodine bonds. The first frontier was enabled by our recent discovery that electrons injected into TiO_2 have a significant influence on the absorption spectrum of surface anchored pigments. More specific objectives in this area include the development of electro-absorption (Stark) spectroscopy as a tool for characterization of molecular-semiconductor interfaces, the quantification of charge screening/ionic reorganization dynamics that accompany interfacial electron transfer, and elucidation of the apparent Gibbs free energy density of states at semiconductor interfaces. The second frontier was advanced by our observation that two distinct mechanisms exist by which I-I bonds can be generated with visible light in fluid solution. We also recently reported the first direct measurements of I-I bond rupture and identified the reaction products. A specific objective in this second frontier is to establish whether these same mechanisms are operative at the sensitized semiconductor interfaces. Additional proposed objectives include analysis with Marcus theory to abstract iodide reorganization energies and standard reduction potentials, design of new molecular compounds that pre-associate two iodides to promote rapid or even concerted I-I bond formation with light, and the correlation of open circuit photovoltages with the magnitudes of surface electric fields and/or the dynamics of I-I bond rupture. The training and education of graduate students is an import aspect of this proposal. The proposed research is directly relevant to dye-sensitized solar cells and is expected to have a broader impact in related fields relevant to solar fuel and electrical power generation; it will provide important molecular-level insights into energy relevant electron transfer reactions that can be driven with sunlight.

First-Row Transition Metal-Based Chromophores for Dye-Sensitized Solar Cells: Fundamental Issues and Applications

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The goal of this research program is to develop chromophores based on first-row transition metal ions for use in dye-sensitized, nanoparticle-based solar cells (DSSCs). The underlying motivation for this research is two-fold. First, since the report by Ferrere and Gregg in 1998 of a functional (albeit low efficiency) device based on a Fe(II) polypyridyl sensitizer there has been little in the way of a concerted effort to further explore the use of first-row transition metal complexes in these devices; such compounds represent a large class of redox-active, synthetically tunable chromophores that have yet to be adequately examined for possible applications in this technology. Second, in order to achieve cost/efficiency ratios in DSSCs necessary for them to compete effectively with fossil fuel-based technologies, it is our belief that multicomponent assemblies will ultimately be required; this (among other reasons) necessitates the use of extremely inexpensive materials for all components of the device. Our program represents the first phase of what we expect will be an expansive effort to examine all aspects of DSSC performance with the notion of using earth-abundant materials as a cornerstone of cell design.

Issues pertaining to the performance metrics of DSSCs can be grouped into three (ultimately interrelated) areas: (1) light management, (2) electron collection, and (3) dark reactions. This project deals primarily with the first issue and builds on our expertise in the application of ultrafast spectroscopic techniques for the study of the earliest events following photon absorption by transition metal charge-transfer complexes. Various steady-state and time-resolved spectroscopic probes – in particular femtosecond time-resolved methods – are being used to characterize interfacial electron transfer dynamics as a function of the composition of the chromophore as well as the driving force for electron injection. The goal of this work is to establish the kinetic framework within which this class of chromophores must operate in order to be effective sensitizers for semiconductor-based photovoltaics. In addition, the thermodynamics and conversion efficiencies of operational solar cells incorporating first row-based sensitizers are being measured in order to forge a link between the steady-state and time-resolved spectroscopic properties of the cells with their performance metrics as a means of identifying which aspects of cell performance require the greatest attention in order to improve overall efficiency.

Our most recent work has been focusing on chromophore design from two different perspectives. First, sub-picosecond time-resolved electron absorption, femtosecond stimulated Raman, and soft x-ray absorption measurements are being exploited in an effort to obtain direct electronic and structural information about the reaction coordinate coupled to this conversion as a guide for ligand design. These spectroscopic studies are being complimented by synthetic efforts to create compounds that target reaction coordinate(s) that we believe may be important for facilitating electronic surface crossings in first-row metal complexes. Second, we have developed a new class of polypyridyl complexes that hold promise for creating an electronic structure manifold in Fe(II) that will effectively resemble what exists in Ru(II) analogs, opening the way for achieving photoredox chemistry in Fe(II) that will allow for interfacial electron transfer in a DSSC device. Finally, since it is not clear that Fe(II)-based chromophores will ultimately prove to be the best choice, we are also developing Cu(I)-based chromophores for charge injection studies. The approach again relies on a confluence of synthetic and spectroscopic studies based on a compositional motif that we believe will circumvent the tendency for these systems to undergo non-radiative decay in favor of interfacial electron transfer.

Monodispersed Zinc Oxide Nanoparticle-Dye Dyads and Triads: Characterization of the Early Events in Dye-Sensitized Solar Cells

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Funding:	$265,000

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 will 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. This research will overcome the problems associated with film heterogeneity through the use of dispersible sensitizer/ZnO nanocrystal (NC) ensembles. Well-defined molecule-like systems will 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, will be used as a dispersible platform to which a variety of new sensitizers will be attached for study using ultrafast spectroscopic techniques.

We will explore dye binding to the ZnO NCs by conducting competitive adsorption experiments using methodology devised during the previous grant period. These experiments will allow us to probe ligand steric and electronic effects, the impact of NC surface curvature and ligand denticity (i.e., monodentate to bi- and tridentate ligands). The goal is to develop a more complete picture of the ZnO NC surface chemistry.

We will develop new tripodal anchoring groups for ZnO NCs that will mitigate the propensity of surface etching by inhibiting chelation at one Zn center. Tripodal carboxylate, pyridine and imidazole ligands will be investigated. Variation of the molecular structure of the tripod and subsequent measurement of its binding constant will help us to probe the structure of the ZnO NC surface.

New dye systems will be investigated. A series of oligothiophenes with systematically varied redox/absorption characteristics will be attached to ZnO NCs with a variety of anchoring groups for ultrafast kinetic studies. Additional dye systems based on Ru, Ir and Cu complexes with variable secondary electron donors will also be synthesized. Finally new low valent isocyanide metal complexes of first and second row transition elements will be tested in preliminary studies for charge injection suitability.

A suite of ultrafast spectroscopic techniques will be used to characterize the excited state and charge transfer dynamics in the new dye molecules and dye:ZnO NC complexes outlined above. Probing from the UV to the near-IR will follow the electronic state evolution. Time resolved Raman spectroscopy will be used to measure changes in structurally specific intra-molecular vibrations, and to probe changes in the bath of intermolecular motions local to the charge transfer. These systems offer the opportunity to investigate the influence of a number of key aspects in these molecular assemblies under well controlled conditions in solution, including the linkage chemistry, distance, geometry, acceptor state density, electronic structure, and energetic alignment.

Ground and Excited State Structures of Sensitizer Dyes Adsorbed on Semiconductor Nanoparticles

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Knowledge of the geometry changes of molecules on excitation and their relation to lifetimes and adsorption of chromophores on substrates is of crucial importance for the design of molecular devices 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. The sponsored research involves synthesis and analysis of crystalline phases of titanium dioxide nanoclusters which reproduce the surface characteristics of the anatase phase. The periodic arrangement of the nanoclusters in these materials allows detailed X-ray diffraction determination of the geometry of the adsorbed molecules in their ground state. Furthermore, the geometry changes of both the adsorbent and the substrate on excitation by light can be determined by use of ultrafast time-resolved pump-probe diffraction methods at picoseconds-resolution. In the latter experiments pulsed lasers are used in conjunction with synchrotron radiation. The structural results are correlated with spectroscopic measurements and theoretical calculations to obtain atomic-resolution understanding of the processes that take place on molecule-coated semiconductor surfaces as a result of light exposure.

The time-resolved experiments make use of polychromatic synchrotron radiation at the Advanced Photon Source. As part of the project experimental and data-reduction methods are being revised to maximize the accuracy of the results and the time-resolution of the experiments.

Fundamental Studies of Energy- and Hole/Electron-Transfer in Hydroporphyrin Architectures

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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.

(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.

Photoelectrochemistry and Electronic Structure of Semiconducting Cu(I)-Niobates and Cu(I)-Tantalates

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Semiconducting metal-oxides have remained of intense research interest owing to their potential for achieving efficient solar-driven photocatalytic reactions in aqueous solutions that occur as a result of their bandgap excitation. The photocatalytic reduction of water or carbon dioxide to generate hydrogen or hydrocarbon fuels, respectively, can be driven on p-type (photocathodic) electrodes with suitable band energies. However, metal-oxide semiconductors are typically difficult to dope as p-type with a high mobility of carriers. Our research is focused on the investigation of new p-type Cu(I)-niobate and Cu(I)-tantalate film electrodes that can be prepared on FTO glass. New high-purity flux syntheses and the full structural determination of several Cu(I)-containing niobates and tantalates have been completed, as well as new investigations of their optical and photoelectrochemical properties and electronic structures via density-functional theory calculations. For example, $CuNbO_3$, $Cu_5Ta_{11}O_{30}$ and $CuNb_3O_8$ were prepared in high purity and their structures were characterized by both single-crystal and powder X-ray diffraction techniques. These two classes of Cu(I)-containing compounds exhibit optical bandgap sizes ranging from ~1.3 eV to ~2.6 eV. Photoelectrochemical measurements of these compounds are currently being performed, and which show strong photon-driven cathodic currents that confirm the p-type semiconductor behavior of $CuNbO_3$, $CuNb_3O_8$, and $Cu_5Ta_{11}O_{30}$. Incident-photon-to-current efficiencies are measured that approach greater than ~5%, with the films exhibiting good resistance to photocorrosion over many hours. Electronic-structure calculations based on density functional theory reveal the visible-light absorption stems from a nearly-direct bandgap transition involving a copper-to-niobium or tantalum (d10 to d0) charge-transfer excitations.

Metal-to-Ligand Charge Transfer Excited States on Surfaces and in Rigid Media Application to Energy Conversion

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Dynamics of excited state processes in thin films and at interfaces are under investigation for the insights that they give into possible photoelectrochemical, photocatalytic, and imaging applications. These studies are based largely on the Metal-to-Ligand Charge Transfer (MLCT) excited states of transition metal complexes of Ru, Os, and Re with polypyridyl ligands. Photophysical properties for a series of Ru(II) and Os(II) complexes such as $Ru(bpy)_3^{2+}$ have been investigated in polyether-acrylate fluids. With addition of an initiator, and thermal or photochemical polymerization, these fluids form optically transparent films on a variety of surfaces. The effect of the fluid-to-film transition on excited state photophysical properties has been documented with a quantitative demonstration of the energy gap law for nonradiative excited state decay. It has also been demonstrated that excited states in these films undergo both energy and electron transfer quenching to quenchers either trapped in the films or incorporated as part of the polymeric network. The distance dependence of electron and energy transfer are being investigated as are the impact of electron transfer traps on long range electron and energy transfer and imaging.

The dynamics of injection and back electron transfer by $Ru(bpy)_2(4,4'\text{-}(PO_3H_2)_2bpy)^{2+}$ and related, polypyridyl-based molecular assemblies on the surfaces of nanocrystalline, mesoscopic TiO_2 films are also being investigated on timescales from psecs to seconds. These experiments are being conducted under conditions appropriate for photochemically driven water splitting into hydrogen and oxygen. Surface dynamics are being evaluated by transient absorption measurements as a function of pH, surface coverage, applied bias, and light intensity under both open circuit and photoelectrolysis conditions. The goal is to establish conditions for maximizing the efficiency of Dye Sensitized Photoelectrosynthesis Cells (DSPEC).

Approaches to Integrated Photochemical Systems for Solar Energy Conversion

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Funding:	$310,000

The primary goal of this project is to understand the fundamental principles needed to develop integrated artificial photosynthetic systems to help satisfy the expected large increases in energy demand in the coming years. Artificial photosynthetic systems for practical solar fuels production must collect light energy, separate charge, and transport charge to catalytic sites where multi-electron redox processes for fuels formation will occur. This project is focused on how to promote and control (1) energy capture, charge separation, and long-range directional energy and charge transport; (2) coupling of separated charges to multi-electron catalysts for fuel formation; and (3) supramolecular self-assembly for scalable, low-cost processing from the nanoscale to the macroscale. To accomplish these goals, this project is investigating how the molecular structure and electronic properties of electron donor-bridge-acceptor molecules determine the transition from the charge tunneling mechanism to the charge hopping mechanism to achieve efficient, long-distance photochemical charge separation. Work is also being performed to determine how covalent electron donor-acceptor building blocks can be optimized to carry out photodriven charge separation and long distance charge transport within self-assembled supramolecular structures by integrating efficient light-harvesting and photodriven charge separation in a single self-assembled molecular array. This project is also investigating how photodriven charge separation systems can efficiently provide charges to multi-electron catalysts for fuels formation. Methods to assemble ordered, integrated photochemical systems on solid supports with a view toward scalability are also being developed. To carry out these tasks, this project is synthesizing new molecules and supramolecular arrays and characterizing their structures using x-ray scattering techniques at the Advanced Photon Source, Argonne National Laboratory. Time-resolved femtosecond transient absorption and vibrational spectroscopy are being used to determine the dynamics of energy and charge transfer in these systems. In addition, time-resolved pulsed electron paramagnetic resonance spectroscopy is being used to probe the structure and nanosecond dynamics of the paramagnetic, charge-separated intermediates created in the fuel-forming reactions. This detailed information is essential to designing integrated molecular systems for photochemical solar energy conversion.

Fundamental Studies of Light-Induced Charge Transfer, Energy Transfer, and Energy Conversion with Supramolecular Systems

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This project seeks to exploit supramolecular chemistry to (a) interrogate and understand fundamental aspects of light-induced charge transfer and energy transfer and (b) construct solar energy conversion systems that make use of unique assembly motifs to address key conversion efficiency issues. There is a particular focus on the fundamental behavior of new light harvesters and on new redox shuttles useable in dye-sensitized systems. Representative recent results are described below.

(1) SUPRAMOLECULAR CHROMOPHORIC ASSEMBLIES

We have been exploring dye systems that allow us to harvest a large fraction of the visible and near-IR spectrum. Our attention has been on highly conjugated porphyrin systems. The best examples of these systems offer much higher extinction coefficients than the standard ruthenium dyes employed in dye cells and much better spectral coverage than conventional porphyrin molecules.

(2) SHUTTLES

An optimal photoelectrode will display (1) electron transport that is fast relative to electron recombination with an oxidized dye molecule or electron interception by a redox shuttle, including “fast” shuttles, and (2) slow transfer of electrons back to the redox shuttle (including shuttles that are otherwise highly reactive). Condition one ensures efficient charge collection and therefore, good photocurrents. Condition two is equivalent to mandating low dark currents and is a requirement for achieving good photovoltages. Much of our focus here is on dicarbollide nickel(IV/III) systems, although other new systems are also under investigation. By presenting only modest reorganization energies, these systems appear to be capable of using much less thermodynamic driving force to regenerate dyes. This behavior opens up the possibility of accessing much higher photovoltages, while leaving photocurrents unaffected. Alternatively, lower driving force requirements should enable dyes with smaller optical gaps to be used. This could enable much higher photocurrents to be obtained, while leaving photovoltages.

Radiation and Photochemistry in the Condensed Phase and at Interfaces

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Students:	8 Postdoctoral Fellow(s), 12 Graduate(s), 16 Undergraduate(s)
Funding:	$4,200,000

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.

Recent advances in these areas include Ab initio and molecular dynamic simulations of water at high temperature are for the first time providing detailed understanding of structure and excited states of hydrogen-bonded radicals such as hydroxyl. Simulations of excited water itself complement very challenging vacuum ultraviolet measurements of the lowest-energy liquid water exciton band to extend our knowledge of this most important fluid. Electron paramagnetic resonance on a microsecond timescale is employed to probe radical structure, reactions, and dynamics in high temperature supercritical fluids.

Size-dependent electronic structures of semiconductor quantum dots are being investigated for their effective utilization in light harvesting assemblies. Interactions between multiple sizes of CdSe quantum dots and semiconducting metal oxides (stannic oxide, titania and zinc oxide) show a strong dependence of apparent electron transfer rate constant on change in system free energy in agreement with the Marcus many state model for electron transfer from a single donating state into a continuum of accepting states. The lack of direct correlation observed between measured electron transfer rates and measured photovoltaic device performance suggests that other loss mechanisms limit the performance of quantum dot sensitized solar cells.

Investigation of radiolytic reactions in water at high temperature and of the decomposition of irradiated water at surfaces gives new information on reactor water chemistry that will aid in extending the lifetimes of our present water-cooled reactors. Hazardous gas production in the radiolysis of resins and plastics is being probed to help ensure safe conditions in separation systems and in permanent waste storage, respectively.

Fluorescence imaging with a diffraction-limited excitation beam and ultrafast transient absorption spectroscopy have revealed the extent of excitation delocalization in self-assembled porphyrin nanorods, indicating energy transport on the µm scale. The rich fragmentation pattern resulting from low energy dissociative electron attachment to gas phase dipeptides is seen to be dominated by the dehydrogenated closed-shell anion of the parent and often indicates peptide bond cleavage. The addition of sodium nitrate to lysozyme crystals during synchrotron-based cryocrystallography increases the dose tolerance by a factor of two as judged from global damage parameters, and significantly inhibits specific structural damage to disulfide bonds. Coupled on-line microspectrophotometry experiments clearly show damage mitigation, while the reconstructed electron density maps illustrate the associated radiolytic reduction of nitrate.

Conjugated Ionomers for Photovoltaic Applications: Electric Field Driven Charge Separatin at Organic Junctions

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The primary objective of the project is to understand the photovoltaic and photochemical properties of new types of organic semiconductor junctions based on asymmetries in ionic or electronic carrier populations. Such sources of asymmetry are of interest to solar energy conversion because they differ from the traditional frontier-orbital off sets found in most photovoltaics based on organic semiconductors. Furthermore, the intentional presence of ionic and electronic carriers provides a means of shaping the electric field profile in ways that may provide further control over photoexcitations, including the generation and separation of charge carriers. Two specific classes of interfaces based on ionically functionalized polyacetylenes (polyacetylene ionomers) are to be studied. The first is the interface between n- and p-doped ionomers. These junctions are analogues of the more traditional inorganic p-n junctions upon which crystalline silicon photovoltaics are based. Methods to precisely control the doping level will be developed, and the current-voltage (light and dark), spectral response, and capacitance-voltage properties of these junctions will be quantitatively compared to traditional p-n junction theory. The second class of interfaces is that between undoped polyacetylene anionomers and cationomers. These interfaces are proposed to become photochemically doped to form an adaptive p-n junction when illuminated. A series of transient and steady-state current-voltage measurements (light and dark) as a function of ion density and light intensity will be conducted to quantitatively test a photochemical doping model being developed. Collectively, the proposed studies will contribute to our understanding of how ionically functionalized conjugated polymers can be used to improve the efficiency of solar energy conversion systems based on organic semiconductors.

Metal-Linked Artificial Peptides as Photoinitiated Molecular Wires and Antennas

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Our long-term objectives are to develop strategies for using the modular units of ligand-substituted aeg amino acids to make heterometallic and heterofunctional assemblies linked by artificial oligopeptides, and to use spectroscopic methods to understand the mechanisms of energy and electron transfer in these model peptide duplexes. We have focused on two general structures: Ru(bpy)3 containing pendant ligand-containing oligopeptides for binding metal ions, and tripeptides containing one or more ligands in a sequence that directs assembly of trimetallic structures for studying the role of structure in this flexible architecture on electron and energy transfer.

Building on our prior work, elaboration of the oligopeptide scaffolds enabled construction of larger and more complex structures by varying the aeg substitution about the Ru complex core. The Ru complex with bound Cu or Pd, and the hetero trimetallic Ru Cu Pd complex have been prepared, fully characterized, and their photophysical properties studied in detail. These structures are particularly important for understanding how to build structures of increasing complexity. This manuscript is in the final stages prior to submission. We conducted additional experiments to understand an earlier observation that binding Zn^{2+} resulted in modest quenching of the Ru chromophore, which was surprising and unexpected. A detailed investigation of the solution structure using NMR spectroscopy elucidated structural changes and dynamics upon binding Zn. These studies revealed changes in the chemical shifts of the protons on the [Ru(bpy)3]2+ complex as a result of binding the Zn ion. Additional experiments have led us to conclude that the primary source of this effect is electrostatic. This manuscript has been submitted and is under review.

In parallel, we synthesized heterofunctionalized tripeptides to begin to understand how to build heteroduplex structures and use these to impart functionality that was not accessible in the Ru structures. For example, palindromic tripeptides containing hydroxyquinoline and bipyridine ligands have been prepared to prepare photo- and redox active structures that have pH dependent formal potentials. The first paper describing the hydroxyquinoline tripeptides will be submitted shortly, closely followed by the study of heterofunctional structures.

Nanostructured Photocatalytic Water Splitting Systems

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This project investigates fundamental problems associated with overall water splitting in molecular photocatalytic systems. Natural photosynthesis provides an existence proof that light absorbing molecules coupled to electron relays and enzymes can drive energetically demanding reactions such as water splitting or carbon dioxide reduction. In natural photosynthesis, the quantum yield for converting absorbed light to chemical products can be quite high because energy-wasting back electron transfer pathways are avoided.

In 2009, this project provided the first demonstration of overall water splitting in a molecule-based system, using dyes coupled to colloidal water oxidation catalysts on porous titania electrodes. Ongoing research in the project involves understanding the dynamics of electron and proton transfer at the semiconductor-dye-catalyst interface. By modifying the structure and components the project seeks to improve the quantum yield, which is currently below 5%, and to extend the spectral range of the photoanode. Another aspect of the project involves the synthesis and study of photocathode assemblies for generating hydrogen from water. These cathode assemblies also consist of photosensitizers and redox molecules, in this case interleaved by oxide semiconductor sheets that are grown layer-by-layer on electrode surfaces. Fundamental questions in this aspect of the work concern current rectification and photodiode behavior in molecular redox chains that are mimetic of photosynthesis. A third problem, which is common to all integrated systems for artificial photosynthesis, is the management of proton flow from the anode to the cathode. In photoelectrochemical cells that produce hydrogen or carbon-containing fuels at the cathode, a membrane is needed to prevent crossover of photogenerated fuel to the anode side of the cell. Unless these cells operate at extremes of pH, charge compensation occurs by migration of buffer ions through the membrane rather than by migration of protons or hydroxide ions. This project is developing membrane/buffer combinations that can sustain the ionic flux at the current density of efficient solar cells without developing high series resistance or large transmembrane pH gradients.

Solvation and Charge Transfer in Ionic Liquids and Polar Solvents

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Ionic liquids are molten salts designed to remain fluid at temperatures below 100°C. During the past decade research into these materials has enjoyed explosive growth as a result of the fact that ionic liquids possess a distinctive combination of properties that promise new solutions to old problems. Prominent among the many uses for which these new materials are currently being explored are energy-related applications such as solar energy conversion, electrical energy storage, CO_2 capture and sequestration, nuclear fuel reprocessing, and biomass conversion. For all of these emerging applications, an understanding of the basic physical chemistry of ionic liquids, their material properties and how they behave as solvent media in chemical reactions, is essential. The research supported under this grant is designed to help establish such a fundamental understanding.

Progress in 2011 has mainly involved completion of two multi-year projects. One of these projects entailed molecular dynamics computer simulations of solvation in a coarse-grained model of an ionic liquid. Using this model we have examined how solute size and charge influence equilibrium solvation energies in ionic liquids and suggested simple approximations for calculating such energies. We have also simulated the dynamics of solvation and exposed the molecular mechanisms responsible for the broadly distributed response characteristics of these high-viscosity solvents. This work also begins to examine translational and rotational friction in ionic liquids in order to help interpret the anomalous dynamics sometimes observed.

The second major project entailed time-resolved emission studies of intramolecular electron transfer reactions. The main focus of this work is to ask whether the same relationships between reaction and solvation times already established in dipolar solvents also apply in ionic liquids. We studied three reactions in which electron transfer, known to be solvent controlled in conventional solvents, and showed that despite the more complex dynamics due to the distributed nature of the solvation response in ionic liquids, there is no fundamental difference between the manner of solvent control over electron transfer in ionic liquids compared to conventional solvents.

In collaboration with the group of Nikolaus Ernsting of the Humboldt University of Berlin, we have also performed greatly improved measurements of the solvation response in a broad array of ionic liquids. In addition to providing the most complete and reliable characterization of this aspect of ionic liquid dynamics, these new measurements have revealed the close connection between solvation dynamics and dielectric response in this type of medium.

Studies of Surface Adsorbate Electronic Structure and Femtochemistry at the Fundamental Length and Time Scales

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We have investigated the femtosecond time scale electron and nuclear dynamics in photodesorption of alkali atoms from noble metal surfaces by time-resolved two-photon photoemission (TR-2PP) spectroscopy 1-3. In the zero coverage limit, alkali atoms chemisorb on metal surfaces in ionic form. Photoinduced charge transfer excitation with ~3 eV photons prepares alkali atoms in their neutral state at the position of the ionic ground state. The strong Coulomb repulsion between neutral alkali atoms and their image charges initiates dissociative wave packet motion. Photoexcitation of the excited state with a delayed 3 eV probe pulse can induce photoemission from the evolving excited state.

In the case of the Cs/Ag(111) system, pump-probe two-pulse correlation measurements (2PC) indicate unusually long lifetime for the 6s resonance of Cs, which make it possible to follow the photodesorption dynamics for several hundred femtoseconds. Below the time zero energy of 6s resonance, 2PC measurements follow nonexponential kinetics that can be modeled with an exponential rise and decay. If we attribute the rise to the nuclear wave packet motion and the decay to the resonant charge transfer from 6s state to the conduction band continuum of the metal substrate, we would conclude that the nuclear wave packet motion as the excited electronic state decays on ~200 fs time scale and the bond length increases by 0.7 Å. The situation is not so simple, however.

2PC measurements as a function of photoemission angle show that the observed kinetics measurements are strongly emission angle dependent. For low-density alkali atoms, one would expect to measure the same excited state population independent of the emission angle. Therefore, the angular dependence must have a different origin, most likely the electron rather than nuclear dynamics. The angle dependence of 2PC measurements arises either from the evolution of the electronic wave function in the intermediate state, or the electron tunneling effects in near threshold photoemission. We are investigating these possibilities by ultrafast photoemission momentum microscopy, at the MPI for Microstructure Physics and by theory.

Construction of High Performance, Low-Cost Photoelectrodes with Controlled Polycrystalline Architectures

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The Grand Challenge for solar fuel production (i.e., the use of solar energy to produce chemical fuels) is to become economically competitive with fossil fuels. Among the various approaches of utilizing semiconductor materials for solar fuel production, the use of photoelectrochemical cells (PECs) for direct water photolysis or reduction of CO_2 is one of the most viable options for low cost solar fuels since both the generation of electron-hole pairs and their use to drive desired chemical reactions are achieved by the same semiconductor electrode (photoelectrode) in a single device. While the construction of highly efficient PECs has already been demonstrated based on single crystal or monolithic electrodes, commercially viable PECs will be most likely designed based on polycrystalline photoelectrodes considering the high manufacturing cost of single crystal electrodes. For developing highly efficient polycrystalline photoelectrodes, it is critical to gain the ability to control various morphological features of the electrodes since they affect the performance significantly. In addition, considering that the semiconductors investigated most intensively to date for use in PECs have been narrowly limited to a few semiconductor types, there is an urgent need to establish facile synthesis methods/conditions to produce a broader range of semiconductors as high quality photoelectrodes. There are several potentially interesting classes of semiconductors that possess proper bandgaps, band positions, charge transport properties and long-term stabilities, which typically have more complex compositions than well studied binary compounds, but they have not been investigated intensively, likely due to a lack of facile synthesis methods that can produce these semiconductors as electrodes with varying features.

The overall objective of the enclosed project is to bring about a marked improvement in the construction, understanding, and available variety of polycrystalline semiconductor electrodes for use in solar fuel production by utilizing electrochemical synthesis methods with the ability to systematically tune the compositions and morphologies of these photoelectrodes. We have already demonstrated during the previous funding period that electrochemical synthesis can offer a new level of precision and freedom in interfacial morphology control that allowed for systematic morphology-dependent studies. For the enclosed project, while continuing our efforts to improve the performance and stability of a few promising binary oxides, we will expand our investigation to various p-type and n-type ternary oxides and dichalcogenides of tungsten and molybdenum that possess visible bandgaps and exceptional long-term stability. We will establish facile electrochemical synthesis conditions to produce these compounds as electrodes with systematically varying compositions and morphologies and study their effects on both the initial performance and the long-term stability. This will significantly broaden our choice of photocathodes and photoanodes that can be used to assemble efficient PECs while enhancing our fundamental understanding of structures and properties of polycrystalline photoelectrodes.

The outcome of the enclosed research will also be beneficial to a broad range of research areas that involve inorganic thin film-type electrodes and/or catalysts for assembling energy production (batteries, fuel cells, photovoltaics) and sensing devices because all electrodes/catalysts for these applications require fine compositional and morphological tuning. Therefore, the proposed work will contribute to the general advancement of basic science related to solar energy conversion and clean energy production/storage.

Understanding Electronic and Atomic Requirements in Catalytic Water Oxidation

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Research effort on this project is currently focused in two primary areas. The first is the preparation and characterization (EPR, XAS at Ru L- and K-edges) of water oxidation intermediates in blue dimer complex and one Ru-based single site catalyst. The second effort involves a development of theoretical approach for analysis of the Ru L2,3-edges XANES spectra of water oxidation catalysts. These are separately described in the following two sections.

ANALYSIS OF SHORT LIVED INTERMEDIATES IN RU BASED WATER OXIDATION CATALYSTS

Using Ce(IV) as an oxidant, we generate reactive intermediates of blue dimer water oxidation catalyst and single site catalyst [RuII(L)(4-pic)2(OH_2)]2+ (1), where L = 4-t-butyl-2,6-di(1',8'-naphthyrid-2'-yl)pyridine and pic = 4-picoline – this is a first reported Ru single site catalysts of water oxidation. Kinetic analysis of the reaction mixtures with the UV-Vis stopped-flow and freeze-quench techniques at millisecond resolution allowed us to determine the times and conditions in which particular reactive intermediates exist and to trap them for further characterization. In the “blue dimer” (pH=1, HNO_3), a highly reactive intermediate with the RuIV,V oxidation states was generated on the time scale of a few seconds. This intermediate reacts with water to form a RuIII,IV species which is spectroscopically different from the stable RuIII,IV product of one-electron oxidation of “blue dimer.” The RuIV,V and RuIII,IV intermediates have unique EPR signals and their oxidation states were assigned from Ru K-edge and Ru L-edges XANES. EXAFS at the Ru K-edge demonstrated changes in the Ru-ligand distances and the angle of the Ru-O-Ru bridge in both intermediates.

In single site Ru catalyst we demonstrated that array of chemical conversions happen on very short time scales even prior to formation of the “RuIV=O” intermediate. We suspect that modification of the coordination environment of Ru center or chemical modification of the ligand takes place prior to or in parallel to the formation of “RuIV=O” intermediate. While formation of the [(L)(4-pic)2RuIV=O]2+ was demonstrated, intermediate with RuV, hypothesized to be a reactive species towards water activation, has not been observed at any tested conditions neither by EPR nor by XAS analysis. Obtained experimental data challenge the current mechanism of water oxidation reaction in single site Ru based catalysts.

THEORETICAL MODELING OF THE RU L2,3-EDGES XANES WITH TWO-COMPONENT RELATIVISTIC ZEROTH-ORDER REGULAR APPROXIMATION (ZORA) IN DENSITY FUNCTIONAL THEORY (DFT)

Attempting the analysis of the electronic structure of Ru-based catalysts of water oxidation by XANES at Ru L2,3-edges we have realized that existing single-electron methods (FEFF, FDMNES) cannot reproduce the details of the experimental Ru L-edge spectra for the $[Ru(NH_3)_6]^{3+}$ model complex nor for the blue dimer. To overcome this limitation we have developed a method to simulate Ru L2,3-edge XANES spectra based on a two-component relativistic zeroth-order regular approximation (ZORA) implemented in DFT. This approach allows for inclusion of spin-orbit coupling effects and results in theoretical Ru L2,3-edge spectra which are in close agreement with experiment. Computational analysis reproduced changes in the white line splitting for studied compounds as well as allowed us to propose that the magnitude of spin-orbit coupling in the Ru 4d level is sufficient to enable considerable mixing of singlet and triplet spin states in the blue dimer. The developed computational approach enhances L-edges spectroscopy as a tool for studies of catalytic mechanisms in 4d transition metal complexes and can be of relevance to other researches in Solar Photochemistry/Catalysis program.

Modular Nanoscale and Biomimetic Assemblies for Photocatalytic Hydrogen Generation

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Funding:	$560,000

A goal of this project is the preparation of nanoscale assemblies for the photocatalytic production of hydrogen (H_2) from water. The modular design of the assemblies allows advances to be made on the modules in parallel by the participating PIs. In addition, modifications can be made to the assemblies to add new functionality in the future. 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.

For module one, a novel biosynthetic method for the preparation of a range of metalloporphyrin-peptide conjugates has been developed. The desired heme peptide is expressed as an N-terminal tag to a cysteine protease domain (CPD) which, upon activation, undergoes autocleavage to yield pure heme peptide. Substitution of the heme iron with zinc results in a photoactive chromophore. The porphyrin-peptides have been attached noncovalently to carbon nanotubes (module two), resulting in nanotube dispersion in water and porphyrin fluorescence quenching. Analysis of energy- and electron-transfer between the porphyrins and nanotubes is underway. Also in module two, vertically aligned carbon nanotubes (VACNTs) have been prepared and porphyrin-peptides attached. Assemblies have been built for measurement of photocurrents in ongoing work.

Research in module three on catalyzing the light-driven generation of H_2 from aqueous protons and an electron source has focused on the design, synthesis and study of metal complexes containing only earth abundant elements as the catalysts. In one study in which a Co dimethylglyoxime (dmg) complex was employed as the catalyst with organic dyes as photosensitizers, the path to H_2 generation was determined to be via reductive quenching and the catalyst was seen to undergo slow decomposition. In another study, Co dithiolene complexes were found to be active catalysts for both photochemical and electrochemical H_2 formation. The Co dithiolene catalysts appear to be relatively robust among molecular catalysts for this reaction and show a high turnover number based on the catalyst (rather than the sensitizer). In another published study, a known Ni complex electrocatalyst studied extensively by DuBois was shown to be effective in the photogeneration of H_2 with very substantial turnover numbers. A different Ni-based catalyst that was investigated is a Ni 2-pyridylthiolate complex that can be generated in-situ. For this catalyst system, greater durability is observed, which is attributed to the avoidance of reductive PS quenching that produces an unstable radical anion. In the Co dithiolene and Ni pyridylthiolate systems, there is evidence for direct ligand participation in the proton reduction mechanism, which is reminiscent of the iron-only hydrogenases.

As alternatives to dyes as sensitizers for H_2-producing catalysts, colloidal semiconductor quantum dots (QDs) have several potential advantages including broad absorption covering the solar spectrum, size tunable band-gap, the ability to store and deliver two electrons, and enhanced photostability. A new development in module three research has been the use of cysteine-capped water-soluble CdSe QDs as the photosensitizer to transfer electrons to a novel Ni catalyst to reduce protons to H_2. The fluorescence of the water-soluble QDs was found to be quenched in the presence of ascorbic acid, establishing this molecule as a potential sacrificial electron donor. Extremely promising results were obtained by mixing QDs and ascorbic acid with a Ni pyridyl thiolate catalyst at pH 9 in a 1:1 H_2O/ethanol solution. Under these conditions, H_2 production occurred with over 100,000 turnovers with respect to catalyst. These preliminary results show that QDs potentially can be used in multicomponent photocatalytic H_2 production.

Currently we have three published papers, one under review, and three to be submitted in the near future.

Photophysics and Photoinduced Charge Transport in Single Walled Carbon Nanotubes

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Funding:	$120,000

Single walled carbon nanotubes (SWNTs) consist of a hexagonal network of carbon atoms (a graphitic sheet) rolled up into a cylinder. The length of these cylinders can be hundreds of microns, while the diameter is ~ 1 nm. Carbon nanotubes are known for their unique mechanical, electrical, and optical traits, which fundamentally result from the strength of the carbon-carbon bond and the effects of quantum confinement around a nanotube’s circumference. For example, carbon nanotubes conduct electricity ten times that of copper for the same diameter. Given their ability to readily accept charge, high aspect ratio, excellent conductivity, and macroscopic size, there has been a significant interest in using carbon nanotubes for solar cell applications, with the general idea that they would assist in the separation and transfer of photogenerated charge to electrodes. However, there has been comparatively very little work on solar cells with NTs also participating in the photogeneraton of charge.

The optical properties of SWNTs make them potentially very attractive as novel materials for light harvesting in solar cell applications. For example, they absorb strongly in the visible and near infrared, (NIR) about 1000 times stronger than a dye molecule. Since Si solar cells do not absorb any of the solar spectrum with wavelengths greater than 1100 nm, SWNTs could absorb wasted NIR light and convert it into usable energy. However, despite recent advances, many simple photophysical properties of carbon nanotubes are not well understood. For example, the relaxation of the SWNT excited state, the origins of the low photoluminescence efficiency, charge transport properties, and the nature of the photoluminescent state are all largely unknown. These and other important photophysical properties must be fully understood before the behavior of SWNTs in solar cell devices can be accurately modeled. Thus this project addresses the general use of novel nanometer scale materials to solve fundamental impediments to further developing cheap and efficient solar energy through studies of the photophysical and photoinduced charge transport properties of single walled carbon nanotubes.

In one project we use ultrafast visible and ultraviolet photons to generate (and detect) multiple electrons in semiconducting SWNTs through charge carrier multiplication generation processes. This project has the potential to make a significant breakthrough, as it will provide a simple route to achieving high overall photon conversion efficiencies from a solar cell that nominally contains only a single semiconducting material. So far, we have shown that one type of nanotube can generate 1.3 electrons per single absorbed blue photon. More importantly our results suggest that nanotubes may be potentially more efficient than other nanoscale materials in terms of overall efficiency in generating multiple charges per absorbed photon.

In a second project, we have acquired fluorescence images from individual SWNTs that are correlated with over 50 topographic atomic force microscope (AFM) images that were "stitched together" covering the exact area of the emitting SWNTs, thereby enabling direct comparison between the two data sets. We determined that only ~11% of all SWNTs were emissive, which strongly suggests that the ensemble fluorescence efficiency (QY) is low (QY ~ 0.3%) because the total population is composed of only a small fraction of bright emitters (bright SWNT QY of ~ 3 % x 11% emissive population). We hypothesize that the low percentage of emissive SWNTs in a typical sample results from the presence of processing defects along the SWNT sidewall, which are introduced when the SWNT is separated from the catalyst support system and during ultrasonic disruption used to separate and isolate aggregated SWNTs.

Femtosecond Fluorescence Microscopy of Nanoparticles in Solar Photoconversion

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We investigated the exciton relaxation and charge recombination dynamics in crystalline polyoxotitanate clusters Ti17Cat4 and Ti17. These materials offer a fascinating intermediate system that spans the gap between single center metal-ligand charge transfer complexes and dye-sensitized anatase nanopartcicle and mesoporous films. In contrast with colloidal anatase, they are perfectly monodisperse and form homogeneous solutions. The emerging picture suggests that the electron- hole pair in the clusters shows some behavior that is common in molecular donor-acceptor systems and some characteristics more typical of dye sensitized anatase. Transient absorption depolarization data suggest that the tightly localized initial polaron undergoes rapid evolution into the fully charge-separated state. The long wavelength spectral component, which we tentatively assign to the injected, electron undergoes very fast depolarization within less than 100 fs. The short wavelength component, which is associated with the localized hole, undergoes much slower, picoseconds depolarization dynamics, suggesting thermally activated hopping between the four degenerate catechol sites. This behavior is typical of dye-sensitized colloidal anatase and dye-sensitized mesoporous films. On the other hand, it was found that the transient spectra and the depolarization dynamics of the Ti17Cat4 are solvent dependent. Such dependence on the polarity and viscosity of the medium is more characteristic of small molecule electron donor-acceptor systems in solution rather than charge injection and recombination at interfaces. Fast pulse radiolysis measurements performed at the LEAF facility at the Brookhaven National Laboratory confirm our preliminary assignment and point to a tight confinement of the excess electron in the Ti17 cluster.

In a separate project we are using femtosecond Kerr-gated fluorescence microscopy which has been developed in our laboratory to study the mechanism of luminescence quenching and enhancement in semiconductor quantum dots on metal surfaces. Hybrid quantum dot/metal nanoparticle/semiconductor substrate systems are of growing interest in solar energy conversion applications. Despite this surge of interest and well-established theories, very little is known experimentally about the ultrafast exciton dynamics at the interface between a chromophore and a metal.

Model Dyes for Study of Molecule-Semiconductor Interfaces and Electron Transfer Processes

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Control of charge transfer between dye-linker-anchor sensitizers to metal oxide (MO) semiconductor interfaces is important for renewable energy projects involving nanostructured semiconductors. However, it is difficult to control effectively the positioning of a molecule on a MO surface, a prerequisite to engineer and study this complex interface. Uncertainty over the binding mode and orientation, and the heterogeneity of the nanostructured metal oxide films can prevail over the molecular design. We designed and synthesized model organic or inorganic chromophore-linker dyes (Ru(II)bpy complexes, porphyrins and organic aromatic hydrocarbons with rigid linkers and multiple anchoring groups to control the binding mode, orientation, aggregation, and electronic coupling of the chromophoric unit onto the surface of the semiconductor. A novel direction of this work is the synthesis and study of chromophores that are shielded from the heterogeneity of the semiconductor nanoparticles by the presence of capping units (strapped and capped porphyrins, the study of which is in progress) or by the symmetric arrangement of rigid ligands (‘star’ Ru(II)-bpy homoleptic complexes).

A series of novel homoleptic Ru(II) star complexes were synthesized as part of a new surface engineering strategy. In the nano-sized, highly symmetrical, star-shaped complexes, the Ru(II) center is coordinated to three identical bipyridine ligands carrying oligophenylenethynylene rigid linker units with (Star-n-BuO) or without (Star) solubilizing alkoxy chains, and terminating with carboxylic anchor groups. The chromophoric Ru(bpy) core cannot come in close contact to the semiconductor surface. The UV-Vis spectra of both complexes displayed intense pi-> pi* bands at lambda ~320 nm, a broad MLCT band at lambda ~ 490 nm, and both exhibited a long lived excited state (lambda PL = 1.2 us). Star-n-BuO exhibited an additional absorption band near 400 nm assigned to a n-> pi* transition from the alkoxy substituents, an enhanced PL lifetime, and an extinction coefficient that was one order of magnitude larger than that of Star. In both cases interfacial electron transfer occurred on unusually slow time scales, and charge recombination was not yet complete in 90 ms. Synthetic modifications, computational studies and binding studies to enhance injection yield are in progress.

Physical Chemistry of Reaction Dynamics in Ionic Liquids

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Students:	4 Postdoctoral Fellow(s), 3 Graduate(s), 1 Undergraduate(s)
Funding:	$650,000

Research in ionic liquids (ILs) has expanded greatly during the past decade for many reasons. Prominent among these reasons is their relevance for energy-related technologies such as solar photo-electrochemical cells and water splitting; fuel cells, next-generation battery technologies and supercapacitors. Understanding charge separation and chemical reactivity in ionic liquids is of key importance for these applications, yet despite the explosion of IL research activity around the world, including some measurements on electron transfer, there has not been a clearly focused program to comprehend all the factors controlling charge transport in ILs and how they differ from conventional solvents. The goal of this project is to study charge separation and electron-transfer reactions in ionic liquids through a wide array of experimental and theoretical methods. Our team of five research groups will work as an integrated unit, exchanging ideas, personnel, and sharing a common set of ultra-pure ionic liquids within the team.

Electron-transfer dynamics and mechanisms will be studied using a range of spectros-copy methods at the university labs combined with pulse radiolysis methods at BNL. Optical methods include ultrafast fluorescence and transient absorption spectroscopy, augmented by state-of-the-art nonlinear optical methods developed by the Blank group at Minnesota. The Margulis group has been developing the theoretical and computational methods to understand the intricate details of the spectroscopy experiments in ionic liquids. Our research team has the capability to prepare, purify, and characterize ultra-purenovel ionic liquids for specific investigations (e.g., those that have electron-donating anions). The physical and chemical properties of the ionic liquids will be analyzed in exquisite detail. We will use standard and state-of-the-art methods, including structural studies using x-ray scattering and diffraction (both at universities and synchrotrons at DOE labs); electrochemistry; and temperature-dependent measurements of viscosity, density, and thermodynamic properties. NMR and conductivity measurements of ion diffusion will characterize the charge mobility in these liquids. A primary outcome from this research project will be the generation of a knowledge base of electron-transfer reactions in ionic liquids, a pre-requisite for a priori prediction of how to apply ionic liquids energy applications. Other benefits to the DOE research mission include union of theory and experiment, which converses structural, dynamical and thermodynamic properties of ionic liquids and chemical reactivity in these liquids. Last but not least, execution of this research work will result in broad-based training of the next generation of physical chemistry researchers with expertise in ionic liquids.

Major participants in this research include the five co-principal investigators listed above, and Dr. Sanjeeva Murthy, a highly recognized expert in x-ray scattering experiments on complex systems. The co-investigators have all worked together in previous and ongoing collaborations. They are recognized for their leadership roles in their respective fields, and in ionic liquids.

Nano-Structured Electrocatalysts for Conversion of Solar Energy to Fuels

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Renewable sources of energy are increasingly needed and solar production of hydrogen fuel from water can contribute if new photocatalyst materials can be identified. To achieve maximum efficiency, the structure/morphology of the photocatalyst is as important as its compositional make-up; both interactively determine optical and charge transport characteristics. The proposed effort focuses on the discovery of nanostructured semiconductor photocatalysts with overall objectives of designing, developing, fabricating, testing and understanding their performance characteristics in systems for solar photoelectrochemical (PEC) production of H_2.

Practical water splitting systems require materials capable of at least 10% efficiency and long-term stability. Ideally, these materials should be stable in aqueous electrolytes under solar illumination, have a band gap between 1.6 and 2.0 eV for maximum light absorbance and sufficient overpotentials to drive the reactions, a conduction band energy negative of the potential for water reduction, and a valence band energy positive of the potential for water oxidation. Metal oxides are excellent candidate photocatalysts for PEC H_2 production systems when modified with dopants selected for structural, light absorbing, catalytic, and ionic charge compensation character. Practically useful PEC semiconducting materials are likely to be complex metal oxides composed of many elements. Considering the astronomical number of multicomponent metal oxides that are possible, combinatorial rapid synthesis and screening are required. Nanostructured morphologies of metal oxide PEC materials also appear to be crucial for efficient employment of visible light since charge carriers would more likely be within the space charge region or readily diffuse to the solid/liquid interface. Multi-material composite structures may also be required to achieve acceptable performance.

We plan to conduct our proposed research through an integrated approach in which discovery and selection of nanostructured electrocatalysts for solar PEC devices are achieved using rapid synthesis and screening tools. The preparation of nano-structured materials that prove promising from rapid screening will be performed via a technique referred to as reactive ballistic deposition (RBD) which enables tuning of photocatalytic and optical properties for high visible-light activity. Employing RBD, films with specific surface areas of up to ~1000 m2/g can be obtained with thicknesses ranging from 0.5 – 10 mm. A broad range of analytical tools will be employed in order to better understand how preparation procedures impact important film properties and photoelectrocatalytic performance. Structural and morphological properties will be characterized by scanning electron microscopy, transmission electron microscopy, spectroscopic ellipsometry, and diffraction techniques [x-ray diffraction and selected area diffraction]. X-ray photoelectron spectroscopy will be used to probe the chemical nature of the films and specific surface areas will be determined by temperature programmed desorption of several probe molecules. A photoelectrochemical cell will be employed to measure several common performance metrics including the incident photon conversion efficiency and the absorbed photon conversion efficiency. AC impedance tests and Mott-Schottky analysis will be used for flat-band and donor density characterization. Ultraviolet-visible spectroscopy will be used to study the optoelectronic properties of the films grown on transparent substrates. Composite oxide semiconductor PEC devices (e.g., “photochemical diodes” and related schemes) will also be constructed and tested.

Single Molecule Spectroscopic Studies of Charge Separation and Charge Transfer

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Funding:	$185,000

A fundamental understanding of the optical excitations and the interactions with charge carriers is critical to many applications with conjugated polymers. Of keen interest are two questions. First, on what length scale can excitons diffuse in these materials? Second, what is the fate of the initial excitations and what fraction lead to separated charges even in neat homopolymers. For both of these questions, we are interested in how these phenomena are affected by solid-state microstructure. We have made recent advances in single molecule/particle spectroscopy that have allowed direct measurement of the energy transfer by examining exciton polaron quenching. In conjugated polymers, radiative recombination of excitons (electron-hole pairs) competes with nonradiative relaxation pathways. We have directed visualized exciton quenching induced by hole polarons in single-polymer chains in a model sandwich device that allows for controlled injection of single charges into the conjugated polymer chain. The distance-scale for quenching was measured by means of a subdiffraction microscopy, —bias-modulated intensity centroid spectroscopy. This technique allows for measurement of the displacement of the emission spot from a single polymer in the quenched state compared with that of the fully emissive polymer. An average centroid shift of 14 nanometers was measured for highly ordered, single-polymer nanodomains in a prototypical-conjugated polymer. This shift requires energy transfer over distances an order of magnitude greater than previously reported for bulk conjugated polymers and far greater than predicted by the standard mechanism for exciton quenching, the unbiased diffusion of free excitons to quenching sites. Instead, we propose that multistep “energy funneling” to trapped, localized polarons is the probable mechanism for polaron-induced exciton quenching. We are now looking at similar centroid displacement in small polymer aggregates built up by bringing polymer chains together using solvent vapor annealing. Using this technique can be smoothly transitioned from the single molecule limit up to the bulk thin film behavior.

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

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Funding:	$120,000

The goal of the project is to develop a set of density functional theory based tools that will provide a way to calculate the charge transfer rates for donor-acceptor molecular systems of practical interest such as porphyrin-fullerene complex. We have developed and refined a method that provides the vertical excitation energies of singly excited charge transfer states which are constrained to be orthogonal to the ground state. We have applied this method to a number of relatively large organic donor-acceptor molecular complexes such as tetraphenyl porphyrin-C60 dyad, Zn-tetraphenyl porphyrin-C70 dyad, pentacene-fullerene dyad, Zn-porphyrin-paracyclophane-Sc3N@C80 triad, carotene-porphyrin-C60 triad etc. For each of these systems a large number of singlet and triplet excited states are calculated. These applications have proved the efficiency and reliability of the method. The next immediate goal is to calculate the forces for these excited states which will be further used to determine the reorganization energies. The goal is to ultimately develop a set of accurate and computationally efficient tools to predict the efficiency of a nanoscale photovoltaic. Determining the rates requires post-processing of accurate electron wavefunctions, the ability to rapidly determine electron-phonon interactions and the role of polarization phenomena. The work described here is a first step toward that goal. In the future these tools will be integrated into one set of tools that can be applied to determine the charge transfer rates for a donor-acceptor heterojunction.

Photoinitiated Electron Collection in Mixed-Metal Supramolecular Complexes: Development of Photocatalysts for Hydrogen Production

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Funding:	$120,000

The growing energy needs of our Nation require that we explore and harness a variety of new energy sources within the coming decades. Fossil fuels are currently used to supply much of our Nation's energy, derived from the sun's energy, as harnessed and converted by plants into biomaterials. The relative rate of fossil fuel use compared to production is a motivating factor for solar energy research.

One attractive alternative energy source is solar energy harnessed without the use of plants. Solar energy conversion is a complex process that requires detailed fundamental understanding and atomic level control of structure as well as energy and electron migration. This project addresses many fundamental issues important for conversion of solar energy into storable and transportable fuels. Large, structurally diverse molecular architectures are constructed with systematic variation of sub-unit identity. This structural control and diversity provides for directed energy and electron flow on the molecular level. Studies of the basic chemical, photophysical and photochemical properties are employed to develop and expand the knowledge base in many fundamental processes important to solar energy capture and conversion. The perturbation of sub-unit properties upon covalent coupling into supramolecules must be understood and controlled for application in solar energy conversion. The supramolecular constructs employed undergo multielectron photochemistry producing H_2 from water. This project develops a deeper understanding of the fundamental nature of the multiple steps involved in the complex processes needed to harness and store light energy. Studies explore and elucidate the factors that promote multielectron photochemistry including the catalysis of the multielectron reduction of substrates to produce transportable fuels such as hydrogen. The structural motifs employ Ru and Os metal to ligand charge transfer (MLCT) light absorbers coupled through polyazine bridging ligands to reactive metal centers, typically Rh. This construct produced the first molecules to photochemically collect reducing equivalents at a metal center and are also able to deliver these reducing equivalents to produce hydrogen from water. These supramolecules contain building blocks to absorb solar light, generate charge separation on a molecular scale, undergo photoinitiated electron collection and catalyze the reduction of H_2O to produce H_2. The coupling of multiple light absorbers with bridging ligands provides for significantly enhanced absorptivity in the UV and visible extending further to the red of typical Ru MLCT light absorbers. This construct has the added consequence of providing supramolecules that are powerful oxidizers in their excited states. The supramolecular architecture allows for sub-unit variation to probe and understand the fundamental properties of these systems and to enhance functioning. Functioning single component systems have been demonstrated with development of a significant knowledge base allowing for substantial increases in photocatalytic turnover and quantum efficiency. Studies continue to expand the necessary knowledge base focusing on the role of device sub-units and excited state dynamics on functioning, the perturbation of sub-unit properties upon incorporation into supramolecular constructs as well as elucidation of the mechanism of functioning.

Membrane-Organized Chemical Photoredox Systems

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Funding:	$130,000

The project has two main interrelated objectives: (1) elucidate the chemical principles that regulate water oxidation catalysis and (2) explore the potential of vesicle-based assemblies in biomimetic approaches to solar-driven water photolysis. In pursuit of objective one, we have been developing advanced photointiated electron transfer and EPR techniques in conjunction with DFT-based theoretical methods to characterize reaction transients detected during O_2 evolution catalyzed by the ruthenium "blue dimer" ($[(bpy)_2Ru^V(O)]_2O^{4+}$). In pursuit of objective two, we have been investigating the prospects of using substituted pyrylium ions to drive photosensitized charge separation across closed bilayer membranes using visible light. In previous work, we have shown that similar ions can rapidly transport electrons across these bilayers via a carrier-mediated electroneutral e-/OH- antiport mechanism. We have also initiated studies to explore ways in which catalyzed water oxidation can be coupled to carrier-mediated transmembrane charge separation and reduction of compartmented reagents.

During the past year, we have published a major review of water oxidation catalyzed by ruthenium complex ions and a DFT computational study demonstrating the feasibility of water addition to 2,2'-bipyridine (bpy) ligands coordinated to highly oxidized ruthenium centers to form "covalent hydrates." Complementary EPR analyses (ENDOR,ESEEM,PEANUT) of a paramagnetic species appearing during catalytic turnover of the "blue dimer" indicate that the signal arises from a S = ½ state with the unpaired spin density residing largely on a single Ru center; moreover the species contains an exchangeable H-atom on the bpy ligand, consistent with it being a "covalent hydrate." Ongoing DFT calculations have resolved issues concerning the strength of electronic coupling between the Ru centers through the oxo-bridging atom, and current studies are focused on calculating activation barriers for water addition to coordinated bpy. Ongoing research in the area of photoinitiated transmembrane redox has been directed at evaluating the prospects that dialkylaminophenyl-substituted pyrylium ions might serve as combined photosensitizers/redox relays to drive charge separation across bilayer membranes using visible light. To date, we have demonstrated that simple pyrylium ions that are photoexcited with near-uv photons are capable of these combined functions, but pyrylium-mediated transmembrane redox using the visible light-absorbing derivatives has only been achieved when a long-lived photoexcited sensitizer (ZnTPPS(4-)) is included in the photoactive system. Manuscripts on each of these topics have been submitted.

Fundamental Studies of Energy- and Hole/Electron-Transfer in Hydroporphyrin Architectures

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Funding:	$145,000

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.

(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.

A Concerted Synthetic, Spectroscopic, and Computational Approach Towards Water Splitting by Heterometallic Complexes in Solution and on Surface

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Funding:	$440,000

In 2009 support was earned from the DOE Office of Basic Sciences through the SISGR-Solar Energy Program to conduct research on multimetallic assemblies for in-bulk and on-surface self-assembled systems. A comprehensive effort is under development at Wayne State University aiming to develop supramolecular multimetallic complexes with integrated acceptor, antenna, and active sites. The understanding of how directional electron transfer and charge separation can be controlled in such systems is a necessary step toward effective water oxidation catalysts. The Verani/Endicott/Schlegel collaborative is using synthetic, redox-, spectroscopic-, surface-, and computation-based techniques to develop new molecular systems capable of photoinduced electron transfer, directional charge separation and surface organization. These properties are fundamental requirements to the development of efficient integrated water splitting catalysts. A progress report follows.

COLLABORATIVE PROGRESS

The collaborative published three papers thus far. Five other manuscripts have been or will be submitted in the near future.

PROGRESS IN THE VERANI GROUP

The Verani group has been working diligently toward the development of new mono and multimetallic species containing manganese(III), cobalt(III), and ruthenium(II) centers aiming to understand their relative properties as active sites, acceptors and antennae, respectively. Similarly, heteromultimetallic species merging two or more of these components have been developed containing [Ru(II)Co(III)] and [Ru(II)Mn(III)] cores, among others. Besides the synthesis, electrochemical, and spectroscopic characterization, the group has been investigating Langmuir-Blodgett and self-assembly of monolayered films. A group of ruthenium(II)-based catalysts containing functionalized terpyridine (terpy) and bipiridine (bpy) has been developed as well. Functionalization of the terpy allows for SAM and LB film formation, whereas bpy modulates reactivity.

PROGRESS IN THE ENDICOTT GROUP

The research during this time period has been largely focused on approaches for the spectroscopic characterization of the lowest energy charge transfer excited states of several series of simple transition metal complexes. This has involved (1) the design of simple series of complexes in which the important properties may be systematically varied; (2) determination of the absorption spectra, emission spectra, excited state lifetimes, and other pertinent properties of the complexes; and (3) computational modeling of the electronic states involved in the absorption and emission spectra.

PROGRESS IN THE SCHLEGEL GROUP

The research during this time period has been largely focused on approaches to study TD-DFT methods for calculating electronic excited states of a wide range of molecules. The first publication comparing oscillator strengths calculated by TD-DFT and wave function methods will be submitted in the near future.

Ultra-Stable Molecule-Surface Architectures at Metal Oxides: Structure, Bonding, and Electron-Transfer Processes

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Funding:	$200,000

Efficient photoelectrochemical charge transfer at surfaces often hinges on the ability to produce stable, hybrid structures that integrate molecular systems such as dyes and/or photocatalysts with inorganic materials, particularly metal oxides. We are developing new, modular surface chemistries to create photochemically active molecular assemblies at the surfaces of metal oxide nanostructures. SnO_2 and ZnO are of particular interest because these materials have electrical properties superior to more commonly used oxides, and because they can be easily as nanoparticles, nanorods, and other nanostructured morphologies.

We have recently succeeded in enabling the Cu-catalyzed azide-alkyne cycloaddition reaction, a form of “click” chemistry to be used as a modular way to link Ru-based coordination complexes to metal oxides, and have demonstrated that the short molecular tethers support fast charge transfer and are highly stable. The click-chemistry approach has also been used to assemble dyadic structures consisting of two different oxide nanoparticles, using molecular chemistry to form nanoscale oxide heterojunctions. In both systems, we use a wide range of surface analytical measurements including XPS, FTIR, and AFM to characterize the formation of molecular adducts at the nanoscale, and link these to electrical and photoelectrochemical measurements such as time-resolved surface photovoltage measurements to characterize the photoelectrochemical charge transfer. Our results show that Ru coordination complexes linked to surfaces via “click” chemistry support rapid charge transfer and have excellent stability. Ongoing work is characterizing the molecular factors that impact photoelectrochemical charge transfer on time scales from seconds to nanoseconds. Finally, we are also exploring the use of ultra-stable surface chemistries to enable the “on-surface” synthesis of more complex photoelectrochemically active surface adducts.

A Combinatorial Approach to Realization of Efficient Water Photoelectrolysis

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Funding: $190,000

The increasing need for carbon free energy has focused renewed attention on solar energy conversion. Although photovoltaics offer an attractive method for the direct conversion of solar energy to electricity, it does not directly produce stored energy or fuels. Direct photoelectrolysis of water has the advantage of converting solar energy directly to hydrogen, an ideal non-carbon energy carrier, by replacing both a photovoltaic array and an electrolysis unit with one potentially inexpensive device. Semiconducting metal oxides could potentially be stable under illumination in an aqueous electrolyte for many years making them the most promising materials for solar water photoelectrolysis. The problem is that no known oxide semiconductor can efficiently carry out this process. We have developed a simple, high-throughput combinatorial approach to prepare and screen many complex oxides for water photoelectrolysis activity.

The approach uses ink jet printing of overlapping patterns of metal oxide precursors, metal nitrate salts, onto conductive glass substrates. Subsequent firing produces metal oxide phases that are screened for photoelectrolysis activity by measuring photocurrents produced by scanning a laser over the printed patterns in aqueous electrolytes. Several promising and unexpected compositions have been identified. We are in the process of optimizing and understanding the physical structure, electronic structure, and catalytic ability of these new photocatalysts.

Highly Oxidizing Excited States

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Funding: $75,000

We continue to develop and characterize a novel class of LMCT photooxidants based on tris-phosphine chelate complexes of d5 metals, Re(II) and Mo(I). Prior investigation revealed short excited state lifetimes (~20 ns) for ethenyl-bridges chelates (dmpe)3Re(II) and (depe)2Re(II) (dmpe = $Me_2PCH_2CH_2PMe_2$, depe = $Et_2PCH_2CH_2PEt_2$) with +2.55 V excited state oxidation potentials. Poor emissivity was found for methylenyl-bridged analogues, which is attributed to a C3 geometric distortion of the octahedral coordination environment. In contrast, the propenyl-bridged complex (dmpp)3Re(II) has been prepared and exhibits significantly-enhanced emission properties that are under current investigation. An extension to isoelectronic Mo(I) tris chelates has been carried out- these systems are much more electron-rich (E(ox) of Mo(0)/Mo(I) ~ -1.6 V) and have an associated excited state oxidation potentials of ~ +1.4 V. The final grant period for this grant will focus on completing the photophysical characterization of this now extensive series of available photooxidants.

Oxomanganese Catalysts for Solar Fuel Production

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Funding:	$590,000

The design principles for efficient heterogeneous photocatalysis remain unclear and are the focus of this project. High-valent oxomanganese (oxo-Mn) complexes have been studied in great detail to understand how Nature makes oxygen 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 goal of this project is 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 synthesize titanium dioxide NPs and anchor-linker-ligand conjugates, develop new methods for surface attachment of catalysts using oxidation-resistant anchors and linkers that are stable in water, develop and apply computational methods to analyze IET and characterize catalytic water-oxidation complexes, and use spectroscopic methods to characterize the photochemistry.

DOE National Laboratories

Hierarchical Photosynthetic Systems

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Funding:	$1,360,000

Subtasks one and three of the Hierarchical Photosynthetic Systems program investigates fundamental mechanisms for coupling photons to fuels in natural photosynthesis and hierarchical, biomimetic photosynthetic assemblies. The program on natural photosynthesis investigates mechanisms that allow photosynthetic proteins to operate as media optimized for energy-conserving, photochemical electron transfer, and maps electron and energy transfer pathways in photosynthetic reaction center and photosystem complexes. The program resolves fundamental mechanisms for solar energy conversion. Subtask three, builds upon these concepts and implements designs for achieving solar photons-to-fuel conversion using supramolecular chemistry and bio-hybrid synthetic approaches. The two opportunities are linked by a shared suite of common supramolecular design, synthesis, and analytical methods. The program tests strategies for the design of photo-catalysts based on biological host-guest chemistry, with sustainable atomic compositions, capable of implementing biological assembly and repair mechanisms, and that can be tailored for integration across biological, organic, and inorganic photochemical and electrochemical conversion devices. A distinguishing feature of this program is the combined use of time-resolved synchrotron x-ray spectroscopy and scattering techniques, ultrafast transient optical techniques, and time-resolved EPR analyses for determining ground and excited state structures and function of biomimetic hybrid architectures for solar chemical energy conversion.

Catalyzed Water Oxidation by Solar Irradiation of Band-Gap-Narrowed Semiconductors

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Students:	6 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$800,000

This project is attacking issues hindering progress in solar-driven water splitting using an integrated experimental and theoretical approach. While empirical studies have demonstrated a number of materials with measurable water-splitting activities, the breakthroughs needed to support a hydrogen economy will require integrated understanding of co-dependent semiconductor and catalyst properties. We address four areas that offer 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 (non-precious) 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-to-catalyst-to-water charge transport.

Physical Chemistry of Reaction Dynamics in Ionic Liquids

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Funding:	$150,000

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 identified by several BES workshops and resonates with the BES Grand Challenges 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. Five research groups are working in a coordinated way to achieve a fundamental understanding of charge transfer and transport in ionic liquids. The work performed at BNL under this collaboration 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.

Reactive Intermediates in Condensed Phase: Radiation and Photochemistry

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$540,000

This project studies fundamental dynamics of charge separation and energy transfer that determine chemical reactivity induced by photochemistry or ionizing radiation. Such processes are important in DOE mission-related fields, including aqueous radiolysis occurring in reactors and fuel cycles, in separations media during fuel processing, and in DNA strand breakage upon exposure to ionizing radiation. This project studies these fundamental events as they occur in real time and relates them to chemical reactions that occur in the bulk and at interfaces. These processes involve exotic chemistry that occurs on an ultrafast timescale (<100 picoseconds). One focus is on the action of ionizing radiation on nano-confined or interfacial water, which has been shown to lead to the formation of copious quantities of detrimental products such as hydrogen, hydrogen peroxide and oxygen by poorly understood mechanisms. In this project we utilize pulse radiolysis to investigate the physio-chemical processes that lead to anomalously high radiolytic yields in nano-confined aqueous systems. Such studies are motivated by the need to better understand the role of such processes in contributing to materials corrosion and stress cracking where nano-confined water is present in complex heterogeneous materials such as clays, metal alloys and concrete used in various components of nuclear reactors and nuclear waste storage structures. This work will improve understanding of materials issues relevant to the next generation of nuclear reactor technology and give insight into the basic charge transfer and radical chemistry that occurs at aqueous interfaces. Connections are also being made to interfacial energy transfer processes important in such areas as dye sensitized solar cells and electrochemistry. This project utilizes the techniques of ultrafast and static x-ray spectroscopy at synchrotron light sources such as APS (Argonne) and NSLS (Brookhaven), as well as ultrafast laser methods, and pulse radiolysis at LEAF (Brookhaven Chemistry).

Solar Fuel Production Catalyzed by Transition-Metal Complexes

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Students:	3 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$743,000

We are pursuing research to enable a promising avenue for fuel production using solar energy to activate CO_2 ('solar fuel'). The focus is on 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-C1, metal complexes with an NADH model ligand, and bifunctional catalysts containing photoactive d6 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 C1 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.

Thermal, Photo- and Radiation-Induced Reactions in Condensed Matter

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Students:	2 Postdoctoral Fellow(s), 3 Graduate(s), 0 Undergraduate(s)
Funding:	$3,570,000

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 Laser Electron Accelerator Facility (LEAF) is an important force in these studies. 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 for BNL researchers and external collaborators and users. The program combines powerful experimental techniques with computation and theory. Recent progress in this program includes the following:

(1) finding and quantitative determination of fast “step” processes for attachment of electrons to conjugated polymers that enable determination of fast charge transport

(2) fundamental radiation chemistry and electron transfer processes in ionic liquids

(3) observation of charge transport over long distances along conjugated polymer chains

(4) investigations of reactivity pathways for nitrogen-containing radicals

(5) resolving major controversy about H atom reactivity toward tert-butanol, an essential radiation chemistry compound

(6) insight into proton-coupled electron-transfer and hydride-transfer reactions in water or organic solvents

(7) binding of small molecules including dinitrogen to metal complexes

(8) investigation of CO_2 photoreduction catalysts in supercritical CO_2 ($scCO_2$) and biphasic ionic liquid/$scCO_2$ solvents for improved efficiency

(9) impressive progress in IR detection for clear identification of intermediates produced by photochemistry or ionizing radiation

(10) finding of much faster transport of excitons along conjugated chains than previously reported in other laboratories

(11) utilization of accelerator and photochemical experimental facilities by many users and collaborators

Photosynthesis and Photochemistry - Chemistry with Near- Infrared Photons

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Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$491,000

The purpose of the project is to develop robust photocatalysts for the synthesis of fuels and chemicals from carbon dioxide and water using sunlight as energy source. Our approach is to assemble well-defined `molecular? inorganic units in nanoporous oxide materials that serve as visible light photocatalysts for demanding redox reactions. Selective synthetic methods are being developed for making atomically defined polynuclear transition metal units that serve as visible light charge-transfer chromophores coupled to multielectron catalysts in silica nanopores. The flexibility of the approach affords units consisting of chromophore and catalytic components with well-matched redox potentials, which is essential for achieving thermodynamic efficiency. Structural characterization of the units by optical, FT-IR, FT-Raman, EXAFS, EPR spectroscopy and high resolution microscopy is accompanied by transient optical absorption studies to elucidate the electron transfer energetics and kinetics of the photocatalytic sites. Elementary reaction steps of water oxidation or carbon dioxide reduction are monitored by time-resolved FT-IR spectroscopy. The mechanistic understanding gained from these studies combined with the electron transfer results guide us in the design of polynuclear sites with improved catalytic efficiency under visible and near infrared light.

Photosynthesis and Photochemistry - Primary Processes in Photosynthesis

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Sr. Investigator(s):	
Students:	4 Postdoctoral Fellow(s), 5 Graduate(s), 0 Undergraduate(s)
Funding:	$575,000

This work aims to the determine design principles used by natural photosynthetic systems to harvest solar energy and perform charge separation. The photosynthetic unit is one of nature’s supreme examples of nanoscale engineering. Application of the design principles to the design and synthesis of synthetic solar energy devices holds great promise. Both energy and electron transfer are ultrafast and require the use of femtosecond spectroscopy for their elucidation. We plan to use nonlinear optical spectroscopy, especially two-dimensional electronic spectroscopy, to elucidate the combined energy, electronic, and spatial landscapes of photosynthetic pigment-protein complexes. We aim to understand the role and significance of quantum coherence in the light harvesting process and reasons why coherence is preserved for relatively long times in photosynthetic systems. The experimental techniques will be developed to reveal specific aspects of the dynamics, for example, through use of different polarizations for the four light pulses involved, and through spectral resolution of signals. Complementing the experimental work will be a theoretical and modeling program aimed at extracting maximum information from experiments, guiding the design of new experiments, and self-consistently including the complete quantum dynamics in the theoretical formalism.

Photoelectrosynthesis Using Silicon Microcrystals, Amorphous Microdomains, and Nanostructures

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Beard, Matt, NATIONAL RENEWABLE ENERGY LABORATORY
Neale, Nate, NATIONAL RENEWABLE ENERGY LABORATORY
Students: 5 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $883,000

BASIC STUDIES AND NOVEL APPROACHES FOR PHOTOELECTROSYNTHESIS

This project studies novel approaches to efficient solar water splitting based on earth-¬abundant and low cost silicon micron and nanoscale structures. These are based on (1) Si micron-¬sized and nanoscale-¬sized patterned segregated cubes to avoid photocorrosive/photooxidative catastrophic failure, (2) macroscale p-¬n junctions between n-¬and p-¬doped nanocrystalline films formed from Si nanocrystals (NCs), and (3) Si nanowires that form p-¬n junctions connected in series electrically but illuminated in parallel. Because of quantum confinement NCs will have bandgaps (HOMO-¬LUMO) that are determined by their size and can exceed their bulk bandgaps (1.12 eV for Si). Thus, the NC bandgaps can range from 1.2-¬2.0 eV for Si NCs with sizes from 10 to 3.5 nm, respectively. Two nanocrystalline p-¬n junctions with two different bandgaps will be formed into tandem type photochemical diode structures to generate sufficient photovoltage to split H_2O. Since it is necessary to dope the nanocrystalline films both n-¬type and p-¬type to form p-¬n junctions an experimental and theoretical investigation of doping in Si NCs is being undertaken.

Subtask H, Photochemical and Photoelectrochemical Conversion of Solar Energy and Novel Nanoscale Science

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Johnson, Justin, NATIONAL RENEWABLE ENERGY LABORATORY
Students: 0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding: $500,000

EFFICIENT H_2 PRODUCTION VIA NOVEL MOLECULAR CHROMOPHORES AND NANOSTRUCTURES

The objective of this research is to establish the fundamental science that will ultimately allow the construction of a high efficiency tandem photoelectrolysis solar cell (photoactive cathode and anode). The highest theoretical photolytic water splitting efficiency requires two photosystems (labeled PSI and PSII) that are coupled such that the two individual photopotentials are additive (like in biological photosynthesis) to generate sufficient voltage to split water into H_2 and O_2. Initial work is focused on generating two electron-¬hole pairs per photon via molecular singlet fission (SF) in novel dimeric chromophores that can sensitize the nanocrystalline TiO_2 cathode for H_2O reduction to H_2, and novel nanocrystalline anodic films that can support quantum dot sensitizers that exhibit efficient multiple exciton generation and can also oxidize H_2O to O_2. Doubling of the exciton production per photon greatly increases the photocurrent and results in a relative maximum efficiency gain of about 33%.

Subtask I, Photochemical and Photoelectrochemical Conversion of Solar Energy and Novel Nanoscale Science

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Students: 1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $250,000

TRANSPORT AND INTERFACIAL PHOTOCHEMICAL PROCESSES: SENSITIZED NANOSTRUCTURED ELECTRODES

This research is directed toward understanding the primary physical and chemical factors that govern photon absorption, charge injection, and electron dynamics in functional sensitized nanostructured-based photoelectrochemical (PEC) solar systems. Current studies are aimed at understanding the effects of illumination geometry, morphology, and environmental factors on the light-harvesting and charge-collection properties of NT and nanoparticle-based DSSCs. The objectives are to understand the principal phenomena controlling the operational characteristics key to efficient and stable sensitized nanoporous, nanostructured PEC systems. The current focus is to develop the basic science for constructing effective photoelectrode architectures for high efficiency photoelectrochemical (PEC) tandem systems.

Subtasks A-D; F-G; Photochemical and Photoelectrochemical Conversion of Solar Energy and Novel Nanoscale Science

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Students:	8 Postdoctoral Fellow(s), 5 Graduate(s), 0 Undergraduate(s)
Funding:	$2,430,000

NEUTRAL, DOPED, AND CHARGED COLLOIDAL SEMICONDUCTOR NANOCRYSTALS AND THEIR ASSEMBLIES FOR EFFICIENT SOLAR ENERGY CONVERSION

This purpose of this research is to gain the basic scientific understanding of the unique size-dependent properties of colloidal semiconductor nanocrystals and their assemblies, in order to learn how to construct novel architectures that have the potential for ultra high efficient and low cost photoconversion systems.

ADVANCED SPECTROSCOPY FOR STUDYING EXCITON RELAXATION DYNAMICS AND ENERGY AND CHARGE TRANSFER IN ORGANIC AND INORGANIC NANOSTRUCTURES

The goal is to characterize in detail the initial events after photoexcitation of inorganic nanocrystals and crystalline organic films. Relaxation of excitons and charge carriers and their migration among chromophores and the environment are crucial for understanding mechanisms of exciton multiplication and free charge carrier formation. The fundamental information gained from ultrafast spectroscopic studies impacts the design of systems to be utilized in efficient solar energy conversion.

SYNTHESIS AND CHEMICAL MODIFICATION OF GROUP IV NANOCRYSTALS

The goal is to design and synthesize Group IV nanocrystals (NCs), with a focus on tailoring their surface, optical and electronic properties for application in solar photoconversion, and to provide chemical expertise to help other projects in the program realize their full potential.

IMAGING OF ENERGY AND CHARGE TRANSPORT IN NANOSCALE SYSTEMS

The goal is to develop and demonstrate new high spatial-resolution time-resolved imaging techniques that enable the study of energy and charge transport in nanoscale systems. To study energetic, surface chemical, and opto-electrical properties of individual quantum systems and superstructures, and to study energy and charge transport in relevant nanoscale supramolecular systems.

NANOSCALE PHOTOCHEMISTRY OF SWNTS

The purpose is to develop synthetic and separation strategies to produce well-identified samples of isolated, type-pure SWNTs with defined diameter, electronic structure, and chirality; to perform fundamental scientific investigations to elucidate the electrical and optical properties of type-pure SWNTs at the single tube and ensemble level and how these properties are affected by interaction with extrinsic entities such as quantum dots/rods, light-absorbing polymers, and molecular chromophores; and to apply the knowledge gained from these fundamental investigations to develop systems with long-lived, charge-separated states that can efficiently convert solar energy into electrical or chemical energy, and to understand the limits of possible energy conversion mechanisms.

PHOTOCHEMISTRY OF EXCITONS AT CONJUGATED POLYMER INTERFACES

The goal is to develop a fundamental understanding of photoconversion processes at nanostructured donor-acceptor interfaces and to understand what properties of the interface promote exciton dissociation and inhibit carrier recombination, to develop a molecular level understanding of the factors that influence and control the interfacial interactions such that the photoconversion processes can be manipulated and optimized, and to develop spectroscopic tools for detecting the presence and fate of photogenerated carriers in order to provide a link between the fundamental, molecular-level photoconversion process and the performance of device architectures. The long-term goal is to advance the development of future-generation solar harvesting concepts through fundamental understanding.

PHOTOCONVERSION PROCESSES IN EXCITONIC SEMICONDUCTORS

The purpose is to extend current conceptual and theoretical understanding of photo-induced charge generation, separation, transport, and interfacial recombination processes in organic semiconductor systems; continue extending the previously-developed theoretical model for molecular semiconductors to the description of pi-conjugated polymers; and develop the concepts and materials necessary to investigate interfaces between p-type acidic semiconductors and n-type basic semiconductors. These novel junctions are complex and so far unstudied either experimentally or theoretically. The coupling of acid-base character to semiconductor interfaces provides a new degree of freedom for studying photoinduced charge transfer and interfacial recombination processes. The purpose is also to continue developing techniques for measuring (1) mobility in the substrate plane, (2) charged defect density, and (3) exciton quenching efficiencies by free carriers and by bound charges.

Fundamental Investigations of Water Splitting of Model Ti02 Photocatalysts Doped for Visible Light Absorption

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Sr. Investigator(s):	Chambers, Scott, PACIFIC NORTHWEST NATIONAL LABORATORY
Students:	2 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$550,000

Development of new energy sources is a major need for the 21st century, and hydrogen has considerable potential as an alternative fuel. In the early 1970s, Fujishima and coworkers discovered that hydrogen could be produced from water electrolysis using electrons photocatalytically generated at TiO_2 electrodes. Their discovery continues to motivate research toward development of TiO_2-based photocatalysts for water splitting, although emphasis is now shifting toward study of visible light active photocatalysts because TiO_2 absorbs little of the solar spectrum. Numerous groups have since shown that ion doping red-shifts the TiO_2 absorption spectrum into the visible. In particular, promising results have emerged recently on a new class of visible-light active TiO_2 photocatalysts doped with anions (C, N, S). This project examines the fundamental properties of heterogeneous photocatalytic water splitting on these ion-doped TiO_2 single crystal surfaces (with and without noble-metal loading). Our objective in this project is to provide fundamental understanding into how doping influences the visible-light absorption properties of TiO_2, how charge carriers from such visible light absorption events participate in surface redox processes, and what is the overall mechanism of the visible light initiated water splitting. Research components of the project include: (1) controlled doping of single crystal TiO_2 substrates and films (anatase and rutile) via molecular beam epitaxy and ion beam implantation, (2) dopant characterization using a wide variety of state-of-the-art techniques (e.g., scanning probe microscopy, photoemission, diffraction and electron paramagnetic resonance spectroscopies), (3) theoretical modeling of the physical and electronic structures of the doped and undoped surfaces using DFT methodologies, and (4) UHV surface science methods to probe the thermal and non-thermal (photon- and electron-initiated processes) of the reaction mechanism, kinetics, wavelength/energy dependence and surface specificity of the visible-light promoted splitting of water. These efforts contribute to long-term objectives of DOE BES toward development of new and improved concepts for solar energy conversion, specifically through the photocatalytic production of hydrogen.

III. SCIENTIFIC USER FACILITIES DIVISION

Institutions Receiving Grants

The Physics of Gain Mechanisms in Free Electron Lasers

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Students:	2 Postdoctoral Fellow(s), 5 Graduate(s), 5 Undergraduate(s)
Funding:	$414,000

The research under this grant has expanded in scope in recent years, well beyond the original mission as stated in the now-dated grant title, which was formulated during proof-of-principle experiments of the self-amplified, spontaneous emission free-electron laser (SASE FEL). Presently, work under BES support emphasizes fundamental beam physics as it underpins phenomena in FELs, and looked increasingly at advanced concepts that impact the next two generations of FEL. These fundamental beam physics topics are increasingly of novel flavor, as we look at time scales of beam and FEL pulses in the attosecond regime. In this new regime, the challenge of creating, manipulating, transporting and diagnosing ultra-high brightness electron beams to drive SASE FELs and other advanced light sources becomes a compelling and intricate enterprise. At UCLA we have been central in the conception and investigation of this new frontier, which now embraces another main activity, that of advanced acceleration techniques; in which we have now begun to work on light sources based on plasma and dielectric accelerators, driven by both beams and by lasers. Finally, we note that in developing new light sources, we have pushed towards proof-of-principle experiments showing the use of new tools such as inverse Compton scattering (ICS), and ultra-relativistic electron diffraction (UED). These activities take place in the context of a coherent educationally-driven program known as Particle Beam Physics Laboratory (PBPL) at UCLA. This program produces a notable fraction of the PhDs granted in the US in the physics of accelerators, beams, and FELs.

Versatile, Programmable Area Pixel Array Detector for Time-Resolved Synchrotron X-Ray Applications

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Funding:	$700,000

It is widely acknowledged that many, if not most, experiments at modern synchrotron radiation (SR) 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 analysis 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.

Maximizing the scientific potential of this new kind of 'smart' detector requires designing a high-speed CMOS front-end and examining each point along the communication chain (from x-ray detection to signal collection and conditioning to FPGA processing to data acquisition and storage) to avoid bottlenecks. Since the design and fabrication of custom, large-format ASICs suitable for area detectors, is inherently expensive it is imperative that each PAD design build on the lessons of earlier work and, in so far as possible, utilize integrated circuit parts that have already been proven to work. Utilizing the past experiences of our detector development group we have been (1) adapting pixel circuits developed in the past to new FPGA controller hardware to realize usable detectors as rapidly as possible, (2) performing R&D on novel FPGA-reliant pixel designs, and (3) implementing the resultant detectors for a wide variety of experimental applications at synchrotron radiation sources.

Key Laser Technologies for X-Ray FELs

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Sr. Investigator(s):
Students: 1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding: $450,000

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 FELs. These facilities will be laser and accelerator combined laboratories that enable optical- X-ray pump probe and imaging studies. In this project, we develop femtosecond and attosecond timing distribution and synchronization systems that will make such facilities fully functional and enable completely new research capabilities. 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. Robust, ultralow noise femtosecond solid-state and fiber sources will be identified or developed to meet the need of attosecond precision timing distribution systems. Timing distribution test beds on the 1 km length scale will be implemented at the sub-femtosecond and eventually sub-100 attosecond level.

Optics for Advanced Neutron Imaging & Scattering

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Students: 0 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding: $282,000

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. The optics is made of axisymmetric grazing-incidence mirrors, such as an ellipsoid, confocal ellipsoid-hyperboloid pairs, or similar. Such systems, known as Wolter mirrors, are commonly used in x-ray telescopes, as produced by the optics group at NASA. The neutron-optics program at MIT is in collaboration with NASA (the NASA group submits a separate Abstract).

The project at MIT has progressed towards three main objectives: (1) design optics for a small-angle neutron scattering (SANS) instrument, such as EQ-SANS at SNS; (2) design optics for high-efficiency neutron flux collection; and (3) develop a concept of a neutron-imaging instrument equipped with focusing mirrors. Accordingly, the design and optimization of SANS mirrors has been finalized. In addition, the optics for collecting the highest possible flux density on small samples is in the process of optimization for SNAP high-pressure diffractometer at SNS. The comparison with existing focusing guides will be made by ray-tracing calculations. A ray-tracing simulation of imaging with Wolter mirrors has been carried out. The recent imaging experiment is described in the accompanying Abstract from the NASA group. Finally, we are getting ready to make test mirrors for an existing neutron-scattering instrument. These mirrors will be used to test the performance of a mirror-based instrument and confirm results from ray-tracing simulations.

Picosecond X-Ray Detector for Synchrotrons

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Sr. Investigator(s):	
Students:	0 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$138,800

A picosecond (ps) is the order of magnitude governing the transfer of energy from a photo-excited electronic system to the underlying lattice, and hence is of fundamental importance in many energy-related systems. The goal of this program is to develop a semiconductor-based x-ray detector that will provide ps time resolution for standard laser pump/x-ray probe experiments at x-ray synchrotron sources. This is important because the synchrotron pulse width of nearly 100 picoseconds prevents reaching the highly desirable 1 ps range, using standard detectors. Progress has been made in two related areas: (1) fundamental studies of ultrafast semiconductor response to x-ray pulses observed by band-gap laser transmission spectroscopy and (2) development of a coplanar stripline (CPS) circuit on GaAs with ps optical sampling.

X-RAY PUMP/OPTICAL PROBE CROSS-CORRELATION STUDY OF GaAs

We discovered how an intense x-ray pump beam transforms a thin GaAs specimen from a strong absorber into a nearly transparent window in less than 100 picoseconds, for laser photon energies just above the bandgap. We find the opposite effect, x-ray induced opacity, for photon energies just below the band gap. These observations raise interesting questions about the ultrafast many-body response of semiconductors to the absorption of hard x-rays, and provide a new and simple approach for constructing an x-ray/optical cross-correlator for both synchrotron and XFEL applications.

COPLANAR STRIPLINE GaAs DETECTOR WITH PICOSECOND OPTICAL SAMPLING

A standard approach for generating THz radiation is to illuminate the gap of a biased coplanar stripline on a semiconductor substrate with a 100 fs laser pulse. The induced electrical pulse shape is then measured by optical sampling via a “pick-up” electrode. Our detector concept is the same, except x-ray synchrotron pulses replace the 100 fs laser pulses to excite the electrical pulse on the coplanar stripline. A synchronized laser still provides the optical sampling in exactly the same manner. We have tested prototype Si and GaAs detectors (fabricated at Purdue) and have investigated reduced carrier lifetimes controlled by 8 MeV proton implantation (at Purdue’s Prime Lab). The first round of measurements at the APS Sector 7 found that the monochromatic x-ray pulses produced very strong and easily measured currents in these devices. We also found strong evidence that the ion implantation was successful in reducing the carrier lifetimes, as desired.

FUTURE WORK

(1) The x-ray pump/optical probe studies are being extended to other semiconductors, and especially to determine if the response from a diffracted monochromatic beam is sufficient to provide ps detection capabilities. If so, this could be used to measure the ps response of optically-induced melting, phase transitions, or near edge absorption changes in various materials.

(2) The coplanar stripline (CPS) detectors will be refined to determine optical configurations with maximum sensitivity to serve as a useful detector for optical pump/x-ray probe measurements. This will be tested on a semiconductor such as InSb to measure laser-induced melting and associated vibrational excitations.

Photocathodes for High Repetition Rate Light Sources (partnership with LBNL, BNL-complementary R&D)

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Students:	2 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$333,000

This proposal comprises a comprehensive program on all critical aspects of the production of the electron beams needed for future user facilities. The focus is on photocathodes for high repetition rate Free Electron Lasers (FELs) and Energy Recovery Linacs (ERLs), including testing SRF photoguns, both normal-conducting and superconducting. Teams from BNL, LBNL and Stony Brook University (SBU) lead this proposal, and will coordinate their work over a range of topics. The work will be carried out using existing facilities and the support will be used for carrying out the research work on these facilities. The program is concentrated in three areas: (a) physics and chemistry of alkali-antimonide cathodes (BNL – LBNL), (b) development and testing of a diamond amplifier for photocathodes (SBU - BNL), and (c) tests of both cathodes in superconducting RF photoguns (SBU) and copper RF photoguns (LBNL).

This work will make extensive use of synchrotron radiation materials science techniques, such as powder and single crystal diffraction, x-ray fluorescence and EXAFS as well as variable energy XPS. BNL in NSLS and LBNL in ALS have many complementary facilities at the two light sources and use of these will be a major thrust of our program and bring our understanding of these complex materials to a new level.

This R&D program will leverage enormous assets at the three institutions. At the synchrotron radiation facilities, we already have most of the analytical tools we need. We need mainly to add systems to allow transportation of samples between deposition chambers and the various tools, and to add some tools to deposition systems when key information is required. In some cases, the facilities have as well as user-scheduled beamlines, facilities for in-house R&D that can be brought to bear on these problems. This should allow us the time to make deep investigations into new materials. In addition, the labs have already made substantial investments in analytical equipment for photocathode research, for example in a photocathode ARPES system at LBNL, in sophisticated deposition systems and UHV transport carts at BNL and the superconducting photoguns at SBU/BNL. This program will mainly provide the funding for staff to fully utilize our entire existing infrastructure to support the BES need for cathode development.

Superconducting RF Electron Gun

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

The University of Wisconsin FEL team is moving forward with the development a 199.6 MHz superconducting RF gun that meets the required specifications for a CW FEL in the soft X-ray region. A three year program is under way, with key procurements in place and installation of the hardware and commissioning in a year time frame.

An SRF electron gun was chosen because it is well suited to the requirements of an accelerator based lightsource. It uses low charge bunches with a high peak current at the exit of the injector to minimize downstream magnetic compression and reduce collective effects. The electric fields on the cathode in an SRF gun are higher than other CW sources (>20 MV/m) resulting in greater ultimate brightness. Finally, the electron bunch pulse repetition rates for SRF guns are only limited by the RF power couplers and HOM suppression, meaning that user beamlines can be driven at megahertz repetition rates by a single source. These features make the SRF gun very attractive at moderate currents compared to other devices proposed. This approach complements programs in room temperature RF guns at LBNL, DC guns at Cornell, and L-band guns in Europe.

The electromagnetic design itself was optimized to produce maximum electric field at the cathode while minimizing the peak electric field in the cavity. This will reduce the possibility of field emission limiting the cavity gradient. Similarly, the peak surface magnetic field was minimized to reduce the possibility of magnetic quench of the cavity. The cavity was also optimized to produce a large integrated field between the cathode and anode gap in order that the gun should have a large exit energy. The overall design produces very bright bunches that have sufficient momentum to use the demonstrated LCLS emittance compensation scheme (gun/solenoid/linac section) as part of the injector for an FEL. The cathode is warm with respect to the cavity. Another feature of the design is a high Tc superconducting solenoid for emittance compensation. Beam exit energy is 4 MeV with a normalized emittance less than 1 mmmrad.

To meet the stringent requirements on the longitudinal distribution of the bunch to avoid density modulations in the FEL, we plan to use self inflating (blow out mode) bunches for the FEL. Blow out mode is a scheme in which a laser pulse that is significantly shorter than the final bunch length is used to create a charge pancake on the surface of the cathode, which then expands under its own self space charge force to an ellipsoidal bunch with uniform charge density.

Major procurements are now in place. Niowave is fabricating the cavity/helium vessel, and Danfysik is responsible for the High Tc emittance compensation solenoid. A variant of the Jefferson Lab 12-GeV low level RF control module will be used to operate the 20 kW solid state RF system that has been delivered. The photocathode laser system has been selected and is scheduled for delivery at the end of the year. A vault area adjacent to the Aladdin synchrotron is currently being refurbished as the home of the electron gun, and there is sufficient space to allow installation of a post-accelerator at a later date. Installation and system commissioning is scheduled for early 2012 with beam testing scheduled for fall 2012.

DOE National Laboratories

Community Petascale Project	
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Funding:	$50,000

As part of the Community Petascale Project (COMPASS), APS is collaborating with SLAC to develop software to allow start-to-end (S2E) modeling of the LCLS in the Main Control Room (MCR). The software will be based on three codes: IMPACT-T, ELEGANT, and GENESIS.

S2E modeling has been performed in the past for LCLS and other FELs. Indeed, it was crucial in designing the accelerator, understanding its performance, and improving its performance. However, translating a working configuration from the LCLS control room to a simulation is still laborious; and hence, the need for this project. The long-term goal is a graphical user interface that will be used in the SLAC MCR to perform on-demand simulations using a modest-sized dedicated linux cluster.

Accelerator Test Facility	
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Funding:	$450,000

The ongoing program of user experiments capitalizes on the unique ATF infrastructure comprising a high-brightness 80-MeV linac and a Terawatt picosecond CO_2 laser employed separately or in combination. Nineteen current experimental activities were presented and evaluated by the ATF Program Advisory Committee at the User's Meeting in October 2010. The Program Advisory Committee was chaired by Wim Leemans of LBNL and included well-known researchers from universities and national laboratories.

ATF systems were operated for a total of 206 run-days during the last 12 months. This included 119 days of experiments that required electron beam only, 67 days of accelerator development and training, 30 days for experiments that exclusively used the CO_2 laser beam, 50 days of CO_2 laser development and training, and 18 days for experiments that required the interaction of electron and CO_2 laser beams. Over the past year, 34 users from 13 institutions have been setting up and conducting their experiments at the ATF. Experimental results for 3 PhDs were collected.

The most important results are summarized as follows:

LINAC ONLY EXPERIMENT

First Observation of Coherent Synchrotron radiation suppression with shielding plates - a very important result for future Energy Recovery Linacs. It is listed as one of the R&D goals defined at the BES planning workshop. The experiment was carried out in collaboration with the Collider Accelerator Division R&D group and the ATF. It was supported with eRHIC funding.

CO_2 LASER ONLY EXPERIMENT

Ion acceleration was researched by a broad international collaboration, including RAL, Imperial College, Strathclide Univ., Ecole Polytechnique, and SUNYSB. The experiment provided the first demonstration of a new radiation pressure regime of proton acceleration and was advantageous due to the extremely good beam quality and fast energy scaling in linear proportion to the laser intensity. Recent ATF CO_2 laser development has offered unique capability to deliver designed and well characterized beam time profiles from a single pulse to multiple pulses with variable spacing and power. This is believed to be crucial in future understanding and advancing the radiation pressure regime.

LINAC/CO_2 COMBINED EXPERIMENT

The Inverse Compton scattering study conducted in collaboration with INF and UCLA capitalized on the high efficiency of an x-ray source created by counter-propagating electron and CO_2 laser beams, a technique pioneered by the ATF. The experiments allowed the demonstration of single-shot femtosecond phase-contrast radiography of biological objects and single-shot Bragg spectroscopy, which were never achieved previously with Compton sources.

Advanced Detector Development for Synchrotron Radiation

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Students:	1 Postdoctoral Fellow(s), 0 Graduate(s), 0 Undergraduate(s)
Funding:	$700,000

The project conducts basic research in the field of advanced x-ray detectors for synchrotron radiation experiments. Our current focus is on the use of novel high integration techniques to allow more functionality to be embedded within the detector itself. As test-cases for these technologies we have chosen two straw-man detectors. One addresses the needs of x-ray correlation spectroscopy, a technique which reveals the dynamics of a sample on the atomic scale. Its detector requirements are not currently satisfied by any commercial detector system and so it is an ideal target for our efforts. The second system aims to provide an x-ray hyperspectral imaging detector (i.e., one which can provide spectrally-resolved images of an x-ray radiation field). A secondary project aims to develop a planar technology similar to that used for monolithic silicon detectors, but based on germanium. Success in this project would open up the design flexibility we have come to accept from silicon sensors to experiments which demand good efficiency at higher energies than the typical 10 keV region where silicon is optimal.

Photocathodes for High Repetition Rate Light Sources (partnership with Stony Brook U, LBNL - complementary R&D)

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Funding:	$335,000

This proposal comprises a comprehensive program on all critical aspects of the production of the electron beams needed for future user facilities. The focus of the program is on photocathodes for high repetition rate Free Electron Lasers (FELs) and Energy Recovery Linacs (ERLs), including testing RF photoguns, both normal-conducting and superconducting. Teams from BNL, LBNL and Stony Brook University (SBU) lead this proposal, and will coordinate their efforts over a range of topics. The work will be carried out using existing facilities; the support will be used for performing the research at these facilities.

The program is concentrated in three areas: (a) physics and chemistry of alkali-antimonide cathodes (BNL – LBNL), (b) development and testing of a diamond amplifier for photocathodes (SBU - BNL), (c) and tests of both cathodes in superconducting RF photoguns (SBU) and copper RF photoguns (LBNL).

This R&D program will leverage enormous assets at the three institutions. This work will make extensive use of synchrotron radiation materials science techniques, including powder and single crystal diffraction, x-ray fluorescence, EXAFS, ARPES, PEEM and variable energy XPS. The two light sources located at the home institutions (NSLS at BNL and ALS at LBNL) have highly complementary facilities; use of these will be a major thrust of our program and will bring our understanding of these complex materials to a new level. At these synchrotron radiation facilities, most of the necessary analytical tools are already in place. The principal requirement is the addition of systems to allow transportation of samples between deposition chambers and the various tools as well as the addition of some tools to deposition systems to obtain key information during cathode growth. In some cases, the facilities have both user-scheduled beamlines and in-house R&D facilities that can be brought to bear on these problems, providing the necessary capabilities to make deep investigations into new materials. In addition, the proposing teams have already made substantial investments in analytical equipment for photocathode research, for example in a photocathode ARPES system at LBNL, in sophisticated deposition systems and UHV transport carts at BNL and in the superconducting photoguns at SBU/BNL. This program will mainly provide the funding for staff to fully utilize our entire existing infrastructure to support the BES need for cathode development.

Beam Dynamics Studies for High-Current Eelectron Linacs

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Funding: $500,000

The aim of this project is to improve our beam diagnostic capabilities by significantly increasing their dynamic range. The ultimate goal here is to be able to measure beam phase space distribution with a large dynamic range and track its evolution through an accelerator. This will allow us a better understanding of beam halo formation and its evolution. Understanding of this will make operation and tuning of accelerator based user facilities more reliable and better understood.

The foundation of many beam measurements is transverse beam profile measurements. Thus in the beginning of the program we are concentrating on this aspect of the beam diagnostics. We are currently in the process of making a physics design of two sets of diagnostics for transverse beam profile measurements. One of them is an imaging system that will take advantage of image intensifiers to increase the sensitivity of the measurements, and by doing so, increase the dynamic range. In particular, we are working now on diffraction calculations on the imaging system that can limit the dynamic range if not taken in to account properly. We are also in the process of searching, comparing and selecting suitable image intensifiers.

The other beam diagnostic that we will implement is a large dynamic range wire scanners. The large dynamic range here is achieved via a detector system that works in "photon" counting mode, such that the primary measurements is the measurement of the counting frequency. While this technique was demonstrated to work well in the past, its typical drawbacks are a long measurement time and dependence on the transverse beam stability. Therefore, we are concentrating here on making this diagnostic as fast as presently can be achieved. This activity is in the engineering design stage.

One of the techniques that will be used for the transverse phase space measurements is the tomographic phase space reconstruction. These measurements are possible at high beam energy when the beam is emittance dominated such that the linear beam optics formalism describes the beam evolution very well. Making the tomographic measurements requires very specific transverse beam manipulation. Ideally we would like to have beam optics that rotate the transverse phase space by an arbitrary angle as the beam propagates from the reconstruction point to the point where the transverse beam profile is measured. Working on this aspect of the future measurements we have implemented a solver that finds the necessary beam optics setup for any arbitrary rotation angle of the phase space with the total range of the rotation at least 180 degrees. In short this is a multi-objective constrained optimization problem. The contrariness is the requirement that the transverse beam size in the transport is sufficiently small to prevent any beam loss and that the quadrupole strength is limited to the practically available one. The solver is calculating the beam optics for the JLab FEL where we plan to do measurements.

SRF Developments for Next Generation Light Sources

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Funding: $900,000

We operate an R&D test facility to study the physics of fourth generation light sources. The BES funded activities are guided by developing user needs for fourth 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 two 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)).

Superconducting Accelerator R&D for Coherent Light Sources

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Funding: $1,800,000

The superconducting accelerator R&D for coherent light sources will focus on development and demonstration of novel cavity designs optimized for coherent light source applications. The cavities will be designed to meet challenging beam dynamics requirements and operate at 4 Kelvin where significant energy savings are possible. Spoke cavity structures will be the primary focus for the cavity design and several will be fabricated and assembled for operation in a test cryostat to fully demonstrate operational machine performance. A cryostat and cryoplant concept will be developed to provide a packaged accelerator design for further developments. Successful cavity designs will be dressed and assembled with auxiliary components and cryogenically tested to measure integrated performance including microphonics, alignment and RF performance. Additionally R&D will be pursued on reducing the cryogenic heat loads for these cavity designs including the application of Nb_3Sn which was developed many years ago and has demonstrated a reduction of a factor of ten in heat load at 4 K. Secondly plasma cleaning of the spoke cavity structures will be developed to reduce the risk of multipacting and field emission and improve the cavity vacuum.

Acceleration Research for a Next Generation Light Source (Development of a VHF Normal Conducting Photocathodes RF Electron Gun)

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Funding:	$1,780,000

This project involves the development of a new concept high repetition rate high-brightness electron source for free electron laser (FEL) and energy recovery linac (ERL) applications. The successful development of such a source will critically impact the performance of future fourth generation light sources when high-repetition rates (> 10 kHz) are required. The basis of the system is a normal-conducting continuous wave (CW) RF cavity in which the electrons are generated by laser-induced photo-emission on high quantum efficiency (QE) photo-cathodes and accelerated by the electric field in the cavity up to approximately 750 keV energy. The cavity has been designed to resonate at about 200 MHz in the VHF frequency region. The choice of VHF allows the resonator size to be large enough that the power density on the structure walls is at a level that conventional cooling techniques can be used when the cavity is run in CW mode. In addition, the relatively long wavelength allows for large apertures on the cavity walls with negligible distortion of the field in the cavity. Such apertures are necessary for achieving high vacuum conductance, allowing for the very low pressure as required by high QE semiconductor cathodes, which are sensitive to contamination. An additional advantage of such a scheme is that it is based on mature and reliable RF and mechanical technology, an important characteristic to achieve the reliability required to operate in a user facility. Achievements in the project include the following:

- The cavity and ancillary components are fabricated and assembled, all cavity systems are complete. The gun is installed and aligned in its final destination in the ALS Beam Test Facility (BTF), and conditioning with full RF power has started.
- Low power RF tests showed a frequency and quality factor in agreement with predictions. Initial vacuum tests demonstrated the vacuum integrity and promising vacuum performance.
- The 120 kW VHF power supply is installed and operational at the BTF.
- The photocathode laser system developed in collaboration with LLNL and UC Berkeley has been delivered and re-commissioned at LBNL.
- The FPGA –based LLRF system is operating, and under further development. Controls will use an EPICS system, and high level controls software is being developed in MathLab and will continue during the beam commissioning.
- Beamline components and diagnostics systems have been fabricated, assembly into the BTF is under way.

- A collaboration with INFN Milano for the fabrication of Cs_2Te cathodes is in place. The cavity load-lock vacuum system is in the final phase of fabrication. The development of vacuum transport and installation systems for the K_2CsSb cathodes is under way at LBNL. Systems for installing diamond cathodes in collaboration with a BNL group are under construction.
- Beam dynamics studies have defined the beamline layout for the beam tests at the VHF gun energy. Work is under way to complete the layout for the proposed second phase of the project where the addition of a small linear accelerator will allow acceleration of the beam to an energy sufficient to measure the brightness of an injector based on the VHF gun.

Advanced Modeling of Accelerators for Next Generation Light Sources

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Funding:	$262,000

We propose to develop an advanced modeling capability for electron accelerator beam delivery systems for next-generation light sources. Building upon an existing parallel 3D beam dynamics simulation package, the IMPACT code suite, we will develop a new parallel, high-resolution, multi-scale method for modeling space-charge effects below sub-micron level that cannot currently be modeled efficiently and adequately. We will also advance the state-of-the-art in start-to-end, 3D, multi-physics modeling capabilities, and will develop a simulation-based parallel optimization capability for accelerator design and operation. In summary, this work will lead to a high-resolution, 3D, multi-physics, advanced computational tool that will allow rapid design of coherent x-ray sources for optimal performance, while minimizing technical risk and cost.

Detector R&D

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Funding:	$700,000

Under the detector R&D program, we develop unique high-speed, high-sensitivity direct X-ray detectors. Serving primarily a soft X-ray community, such detectors must have low noise and ultra-thin entrance windows. We have deployed hundreds-of-frames-per-second systems at ALS, APS, and LCLS and are prototyping concepts to increase readout speed by two to three orders of magnitude. To ensure the highest quantum efficiency at lower X-ray energies, we are performing R&D on implantation and annealing techniques.

Higher-speed readout not only improves efficiency (fewer wasted X-rays) but enhances the observation of dynamics, tomography, and scanning microscopies. With sufficient speed and sensitivity to record single photons, spectroscopy and sub-pixel spatial resolution become possible.

Photocathodes for High Repetition Rate Light Sources (partnership with Stony Brook U, BNL - complementary R&D)

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Students:	1 Postdoctoral Fellow(s), 1 Graduate(s), 0 Undergraduate(s)
Funding:	$333,000

The project is a collaboration with Lawrence Berkley National Laboratory (Dr. John Smedley and Dr. Ilan Ben Zvi) and Stoneybrook University to develop alkali antimonide photocathodes for high repetition rate photoguns for high repetition rate light sources. The work at LBNL in collaboration with our BNL colleagues, so far has focused on the manufacture and characterization of K2CsSb cathodes. We have achieved 6% quantum efficiency, a factor of 1,000 times the efficiency of metallic cathodes typically used in high gradient photoguns. We have done this while achieving a significantly lower emittance (0.36 microns/mm rms) than achieved with metallic cathodes. During the course of this work we have invented a new method for measuring transverse emittance of electron beams that allows measurements of the complete distribution of momentum to be obtained within msecs. In addition we have started a program of trying to understand the growth and chemical properties of these materials using synchrotron based x-ray diffraction together with XPS. Using these tools we are starting to understand the crystal structure evolution of these materials and the evolution of nanoroughness. Roughness leads to an increase in transverse momentum. We have measured this effect in our momentum measurements at high field gradient and are able to correlate measured nanoroughness to models of the effect on emittance. The next steps in this project will refine the diffraction measurements, improve a greater range of stoichiometry and allow transfer of cathodes into superconducting and VHF high field photoguns. We will also start work trying to grow ordered surfaces and explore the possibilities of lower emittance through use of band to band transition directionality.

Accelerator R&D for a Soft X-Ray Free Electron Laser: Echo Enabled Harmonic Generation

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Students:	1 Postdoctoral Fellow(s), 2 Graduate(s), 0 Undergraduate(s)
Funding:	$1,779,000

The Echo-7 experiment is aimed at demonstrating the Echo Enabled Harmonic Generation (EEHG) FEL seeding technique [G. Stupakov, Phys. Rev. Lett., 102: 074801 (2009)]. EEHG is believed to be one of the most promising approaches to seeding a soft x-ray FEL at nm wavelengths with GeV energy beams. The

Echo-7 R&D effort approached the problem along two paths: (1) there was a theoretical and simulation effort aimed at understanding the detailed beam dynamics and sensitivities of the EEHG approach and (2) there was an experimental effort aimed at demonstrating the technique at wavelengths of a few hundred nm with 120 MeV beams and performing detailed benchmarking of the simulations against the experimental results to provide confidence in extrapolating to shorter wavelengths.

The Echo-7 experiment is installed at the NLC Test Accelerator (NLCTA) facility. The NLCTA is an X-band linac that was built in the early 2000's and since then has supported the E-163 laser acceleration program, high gradient X-band structure testing and testing of ILC rf components.

To implement the Echo-7 experiment, we rebuilt the last 25 meters of beamline. We installed an additional X-band accelerator structure and rf power system (X2) to double the beam energy from 60 MeV to 120 MeV, as well as two undulators (U1 and U2) where the beam would interact with lasers to modulate the beam energy, three chicanes, and additional diagnostics to characterize the performance, including eight new OTR screens. The first chicane (C0) allows one laser to be brought onto the beamline, the two following chicanes (C1 and C2) provide the dispersive paths necessary to rotate the longitudinal phase space. In addition, we installed a new beam energy spectrometer with a resolution of <10-4, a UV vacuum spectrometer for characterizing the radiation spectrum, and two X-band transverse deflecting cavities (T11 and T27), one to characterize the longitudinal phase space and the other to increase the beam slice energy spread which is needed to illustrate the potential of the EEHG technique.

We have developed techniques to cleanly separate the EEHG and the HGHG signals and have systematically benchmarked the EEHG physics by varying the beam optics, beam energy, energy spread and beam emittance to compare against simulation predictions allowing one to extrapolate to much higher harmonic numbers as needed for a soft x-ray source. The experiments have shown the viability of the EEHG concept and the ability to use beam energy modulations that are small compared to the beam energy spread to generate high harmonic seeding which is not possible with HGHG or similar techniques.

The Echo-& R&D effort has been very successful. We have demonstrated the EEHG principal and we have developed a much clearer theoretical understanding of all external seeding approaches. The R&D program has produced 11 journal articles and 9 conference papers.

The NLCTA and the Echo-7 beam line is an excellent facility to continue studies of beam dynamics critical for future FELs. We plan to continue to test the EEHG seeding concept at higher harmonic numbers where the beam optics and collective effects may become more important. To do this, we will upgrade the existing NLCTA injector to provide higher brightness beams which will allow us to study limitations of the EEHG technique with greater sensitivity as well as study a number of other beam physics topics important for future FELs.

First, we will upgrade the NLCTA bunching system to improve the beam longitudinal phase space allowing us to attempt to extend the EEHG demonstration to the 14th and 21st harmonics. We would also use the existing hardware to demonstrate narrow-band and broad-band THz generation and perform detailed studies of the micro-bunching instability, which is a limitation in the LCLS and likely will be in other FEL facilities.

Next, we propose to further upgrade the injector of the NLCTA to increase the bunch charge and improve the beam emittance by a factor of 10 to the sub-micron level. This upgrade would enable higher harmonic generation with EEHG, studies of alternate advanced seeding concepts, higher resolution on the micro-bunching instabilities and studies of CSR emittance growth, and study of emittance exchange. We would also use the facility to test undulator technology such as mm-wavelength undulators being developed at UCLA and rf undulators being developed at SLAC, as well as other diagnostics techniques that have the potential to provide detailed resolution of the longitudinal phase space which will be critical to optimize operating parameters at future FELs.

ACE3P - Electromagnetic Computer Modeling

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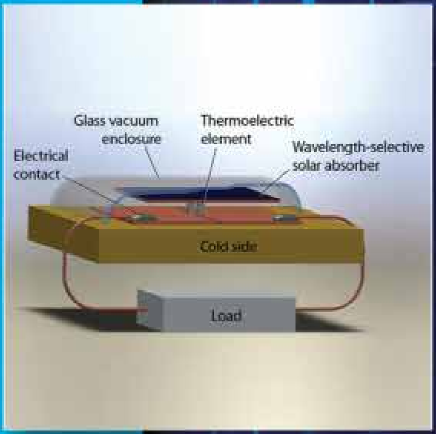
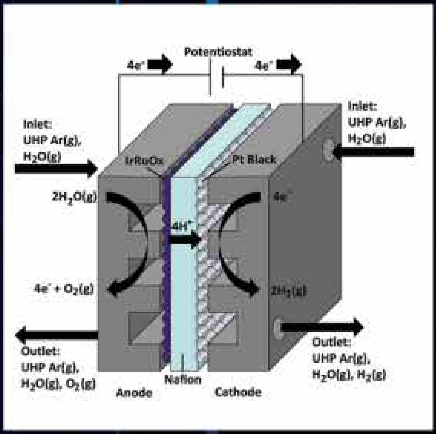
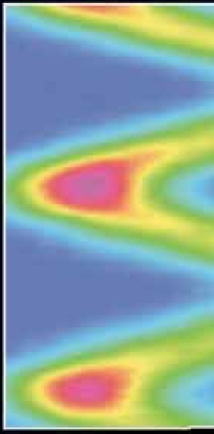
Funding:	$50,000

Under the support of the SciDAC program, SLAC has developed a comprehensive set of parallel electromagnetic codes for accelerator modeling. The simulation suite, ACE3P, employs the high-order finite-element method on unstructured grids for high-accuracy and high-fidelity modeling of complex accelerator structures. Its parallel implementation allows large problems to be solved with high resolution through increased memory and linear speedup. ACE3P's simulation capabilities include cavity design and optimization, wakefield computation, dark current and multipacting simulation, particle-in-cell rf gun modeling, and multiphysics analysis comprising rf, thermal, and mechanical effects. The simulation modules of ACE3P have been applied to several BES accelerator projects.


Glass vacuum enclosure
Thermoelectric element
Wavelength-selective solar absorber
Electrical contact
Cold side
Load


Potentiostat
4e⁻
4e⁻
Inlet: UHP Ar(g), H₂O(g)
Inlet: UHP Ar(g), H₂O(g)
IrRuOx
Pt Black
2H₂O(g)
4e⁻
4H⁺
4e⁻ + O₂(g)
2H₂(g)
Outlet: UHP Ar(g), H₂O(g), O₂(g)
Outlet: UHP Ar(g), H₂O(g), H₂(g)
Anode
Nafion
Cathode



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