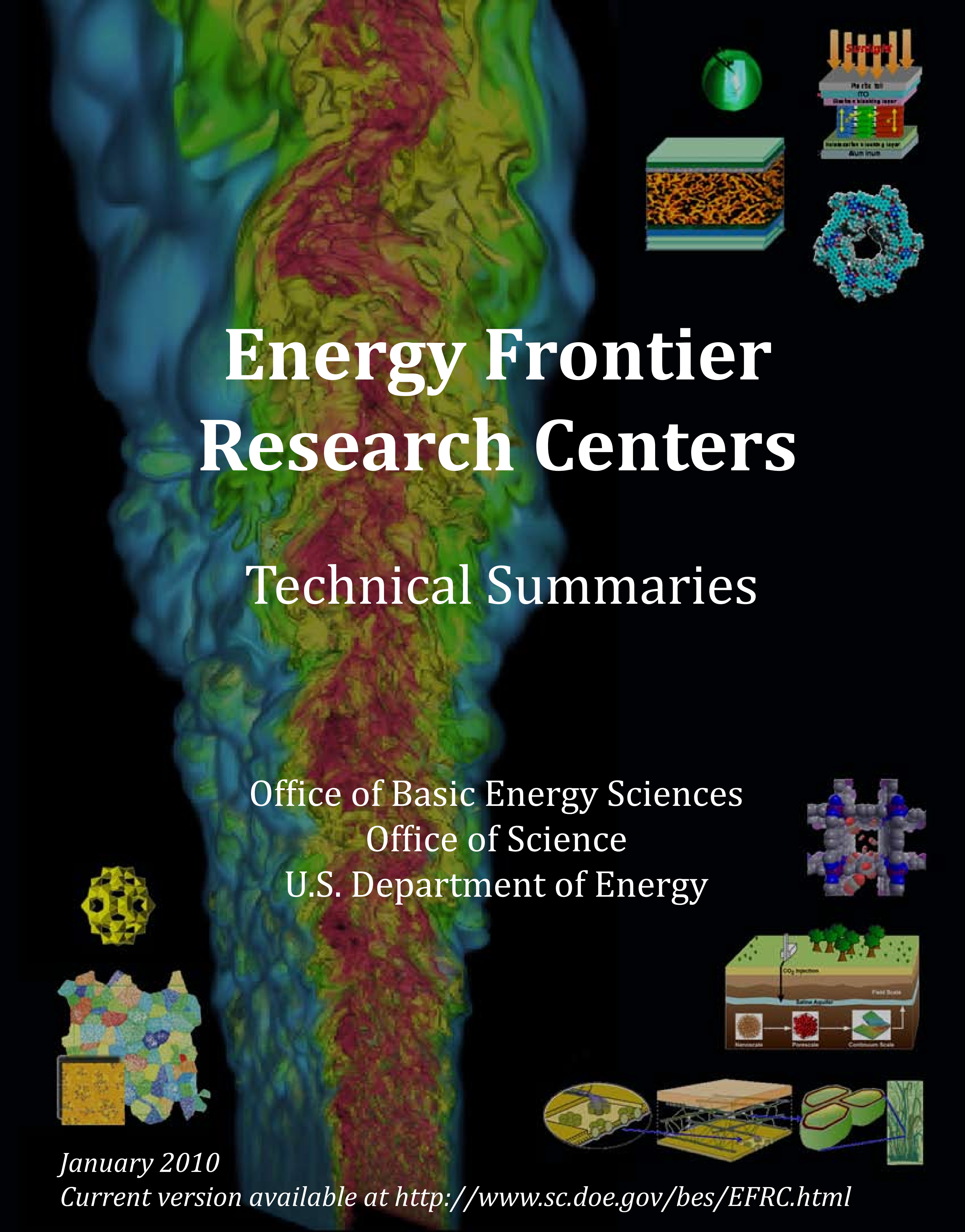

Energy Frontier Research Centers

Technical Summaries

Office of Basic Energy Sciences
Office of Science
U.S. Department of Energy

January 2010
Current version available at http://www.sc.doe.gov/bes/EFRC.html

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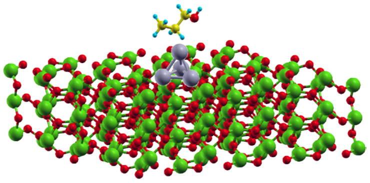

Institute for Atom-Efficient Chemical Transformations (IACT)

The Institute for Atom-Efficient Chemical Transformations (IACT) focuses on advancing the science of catalysis for the efficient conversion of energy resources into usable forms.

IACT is a partnership among world-class scientists at Argonne National Laboratory, Northwestern University, University of Wisconsin-Madison, and Purdue University. Using a multidisciplinary approach involving integrated catalyst synthesis, advanced characterization, catalytic experimentation, and computation, IACT will address key chemistries associated with clean, efficient utilization of the two main chemical energy resources in the United States, namely coal and biomass. We have identified the efficient removal of oxygen from biomass and coal and the hydrogenation of these systems as key chemistries and unifying themes for IACT.

Nature's catalysts — enzymes — show how amazingly efficient chemical transformations can be. IACT researchers believe that the control, efficiency, and selectivity of chemical conversions comparable to those achieved by Nature are within the reach of synthetic catalysts. This achievement will require new catalytic materials, and a major IACT emphasis is the design and synthesis of new, complex, multisite, multifunctional catalytic materials offering new paradigms for catalysis.

To understand these new catalytic materials, an integrated characterization effort is required. In some cases, important questions about catalyst structure, composition, and function can be answered only through advances in measurement science, and this is an important aspect of IACT research. Closely coupled interpretation, understanding, and prediction of experimental results by computation is also critical to advancing catalysis science and is a major IACT activity. Finally, the ultimate validation of our synthesized, characterized, and computationally modeled catalysts will come from characterizing their catalytic performance, as will feedback for further catalyst design.

Thus, IACT may be viewed as consisting of four distinct but intimately interlinked task areas: synthesis, characterization, computation, and chemical and catalytic reaction science.

The leaders of each subtask area are experts in the disciplines constituting its activities. For example, in the synthesis task area, both molecular and materials synthesis are required, and each leader is expert in one of these areas. The integration and interdependence of subtasks follows naturally from the needs that each has for the others to answer basic scientific questions. This integration and interdependence is ensured by an effective management structure whose membership cuts across subtask expertise, and through regular communication via meetings, seminars, and collaborations.

Catalyst Synthesis

IACT researchers will concentrate on three primary classes of materials:

- ***Isolated Mono-Functional Sites***
  Conventional picture of heterogeneous catalysts, such as oxide-supported metal particles or an acid/redox site on a bulk oxide.
- ***Proximate Multi-Functional Sites***
  Catalysts in which multiple functions, such as metal and acid, are positioned in three dimensions with separations on the nanoscale or less.
- ***Synergistic Multi-Functional Sites***
  Catalysts with two or more surface functionalities are in such close proximity that they act simultaneously on a single functional group in the reactant molecule.

Synthesis will seek to control not only the chemistry of the active site but also the geometrical and chemical nature of the support that anchors these catalytic moieties. IACT scientists believe that control of both the active site and the support are necessary to provide catalysts that mimic natural enzymes.

In Situ Characterization

IACT researchers will investigate synthesized materials under "real world" conditions, studying the atomic-scale processes that control catalysis. This task will provide insights to develop physically based predictive models of the property of materials synthesized. *In situ* characterization will employ a variety of spectroscopic tools to provide fundamental understanding regarding why the superior catalysts perform so well and why inferior materials fail completely or deactivate too quickly.

Computational Modeling

Computational modeling will provide theoretical insights at the atomistic level regarding the catalytic properties of new materials and experimental observations. Modeling will also provide guidance in the discovery of new catalytic materials.

Catalytic and Chemical Reaction Science

Catalytic and chemical reaction science will provide data on how the synthesized materials control the fundamental chemistry of oxygen removal from carbohydrates, lignin, and lignite. Since the reactants in transformations are multi-functional molecules, selective transformation of one function but not another will be critical to developing and exploring efficient chemical conversion processes.

Institute for Atom-Efficient Chemical Transformations (IACT) Personnel	
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Northwestern University	**P.C. Stair (Deputy Director)**, L.J. Broadbelt, M.C. Kung, T.J. Marks, S.-B.T. Ngyuen, J.W. Notestein, K.R. Poeppelmeier, E. Weitz
University of Wisconsin at Madison	J.A. Dumesic, T.F. Kuech, C.R. Landis, M. Mavrikakis
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Center for Electrical Energy Storage (CEES)
EFRC Director: Michael Thackeray
Lead Institution: Argonne National Laboratory

Mission Statement: *The Center's overarching mission is to acquire a fundamental understanding of interfacial phenomena controlling electrochemical processes that will lead to a dramatic improvement in the performance of electrical energy storage devices, notably batteries and supercapacitors.*

Batteries and electrical energy storage are central to any future alternative energy paradigm. In the realm of energy generation, future sources are likely to be intermittent, requiring storage capacity during quiescent times. In the realm of energy use, batteries are the likely long-term storage solution of choice. The growing reliance on lithium batteries, in particular, for consumer electronics-, aerospace-, defense-, telecommunications- and medical applications, and ultimately stationary energy storage for uninterrupted power supply units, the electrical grid, and transportation will continue unabated. Of all systems, rechargeable lithium batteries offer the greatest chance for breakthrough opportunities and, in time, these batteries are destined to constitute a "lithium economy".

While lithium-ion batteries have been successfully implemented in relatively small devices, such as cell phones, laptop computers and cordless power tools, the entry of this technology in heavy duty systems, such as hybrid electric vehicles (HEVs) and 'plug-in' hybrid electric vehicles (PHEVs), has been slowed by barriers relating to calendar and operating life, safety concerns and cost. The performance limitations arise largely because of uncontrolled reactions that occur at high and low potentials at the electrolyte/electrode interface, which lead to a high cell impedance, reduced energy and power output, and a limited cycle life (<2 years). While electrode/electrolyte interfaces and interfacial processes constitute weak links in *all* electrical energy storage devices, these corrosive reactions are not always detrimental to the operation of batteries and supercapacitors—they can also act positively to create passivating, protective layers that allow rechargeable reactions to occur repeatedly over many electrochemical cycles. *Control and understanding of the composition and structure of electrified interfaces, which is core to the mission of this Center, are essential to overcoming present-day limitations and providing the fundamental basis for finding breakthrough technologies for the next generation of electrical energy storage devices and beyond.* Success in this endeavor will allow the design of a new generation of materials that can operate safely at high and low potentials and provide, uncompromisingly, the necessary increases in energy and power to enable an improved fuel economy and the emission benefits of HEV and PHEVs, and a reduction on the nation's dependence on foreign oil.

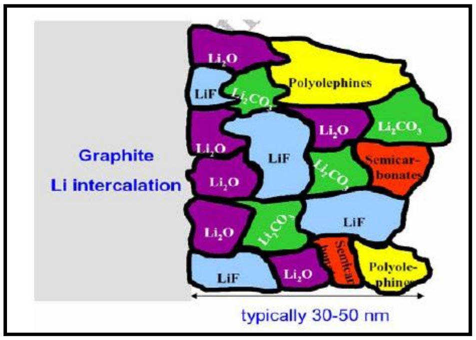

Figure 1. Schematic depiction of a solid-electrolyte interface ("SEI" layer)

Previous work has emphasized the role of the Solid-Electrolyte *Interfaces* and *Interphases* (collectively, the "SEI" layer) as critical components in electrochemical energy storage. An "SEI" forms in response to the thermodynamic instability of the electrode-electrolyte interface, creating a complex heterogeneous 3D collection of secondary phases and insulating layers having many solid-liquid and solid-solid interfaces (Figure

1). SEI layers have dynamic evolving structures characterized by transverse and longitudinal heterogeneities and compositional and structural gradients. The dynamic creation of “SEI” layers at electrode-electrolyte interfaces by complex potential-dependent and concentration-dependent processes leads to a weakened, defect-laden structure that is the singular factor which limits the safety, performance, and capacity of present day battery constructs.

The Center is organized around three individual, but strongly interconnected subtasks in electrical energy storage; they address common issues of electron transfer, dynamics of cation and anion transfer at the electrode-electrolyte interface, and the interplay of materials and architectures at all length and time scales.

Subtask 1: Three-dimensional architectures at the electrode/electrolyte interface

This subtask focuses on the design and electrochemical evaluation of three-dimensional electrode/electrolyte interfaces using novel scaffolds, nano-architectures and surface structures; the task includes experimental studies and theoretical modeling of anode/electrolyte and cathode/electrolyte interfaces.

Subtask 2: Dynamically responsive interfaces

This subtask focuses on microcapsules and electrolyte additives to improve battery safety and longevity. Major activities include: 1) Engineering of microcapsule shell walls to protect core contents and release core contents with an appropriate triggering mechanism; 2) Developing encapsulated phases for electrode shutdown (battery protection) and damaged electrode restoration; 3) Theory and modeling to design and select suitable microcapsule and electrolyte additives; and 4) Testing functional responses of microcapsules, healing agents, electrolyte additives (including redox shuttles and those forming stable passivating layers on the electrodes).

Subtask 3: Understanding and control of interfacial processes relevant to the “SEI”

The central focus of this subtask is the characterization of “SEI” layers and architectures relevant to the processes that limit the performance of energy storage materials, such as materials strain due to lattice expansion due to Li incorporation, the role of lateral heterogeneities, the breakdown of solvent molecules at elevated potentials, and the role of additives in stabilizing the interface. The initial focus will be to develop an in-depth understanding of 1) surface structures by *in-situ* characterization, 2) processes associated with “SEI” structures and their formation, and 3) the role of passivating layers in extending materials’ performance.

The Center brings together a world-class team of 17 scientists from Argonne National Laboratory (ANL), the University of Illinois at Urbana-Champaign (UIUC) and Northwestern University (NU) who will leverage BES user facilities at Argonne, i.e., the Advanced Photon Source, the Center for Nanoscale Materials, the Electron Microscopy Center for Materials Research and the Argonne Leadership Computing Facility. Facilities at UIUC include the Center for the Microanalysis of Materials and the School of Chemical Sciences Facilities; NU’s facilities include the Nanoscale Characterization and Experimental Center.

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University of Illinois, Urbana-Champaign	A. A. Gewirth, D. D. Dlott, J. S. Moore, R. G. Nuzzo, N. R. Sottos, S. R. White
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Center for Bio-Inspired Solar Fuel Production
EFRC Director: Devens Gust
Lead Institution: Arizona State University

Mission Statement: The goal of the Center is to use the fundamental principles underling photosynthetic energy conversion to design artificial constructs that use sunlight to oxidize water, and combine the resulting high-energy electrons and protons to yield hydrogen gas efficiently.

The need for a continuous energy supply and energy requirements for transportation necessitate technology for storage of energy from sunlight in fuel, as well as conversion to electricity. Cost-effective technologies for solar fuel production do not exist, prompting the need for new fundamental science.

Fuel production requires not only energy, but also a source of electrons and precursor materials suitable for reduction to useful fuels. Given the immense magnitude of the human energy requirement, the most reasonable source of electrons is water oxidation, and suitable precursor materials are hydrogen ions (for hydrogen gas production) and carbon dioxide (for reduced carbon fuel production). Natural photosynthesis harvests solar energy on a magnitude much larger than that necessary to fill human needs. It does so using antenna-reaction center systems that collect sunlight and convert it to electrochemical energy via formation of charge-separated species. This electrochemical potential is coupled to an enzymatic catalyst for water oxidation and to catalysts for reductive chemistry that produce biological fuels such as carbohydrate, lipid, or molecular hydrogen.

The Center will approach the design of a complete system for solar water oxidation and hydrogen production by applying the fundamental design principles of photosynthesis to the construction of synthetic components and their incorporation into an operational unit. The functional blueprint of photosynthesis will be followed using non-biological materials.

Collection of sunlight and conversion to electrochemical potential will be performed by *artificial antenna-reaction centers* based on their natural analogs. These will be constructed using the tools of organic chemistry and components such as porphyrins, fullerenes, and carotenoid polyenes. They will incorporate light harvesting (absorption and energy transfer), charge separation (photoinduced electron transfer), photoprotection and regulation.

Water oxidation complexes will be based on a unique, self-assembling, engineered DNA nanostructure that organizes short synthetic peptides arranged in a manner analogous to the natural oxygen-evolving complex. These peptides will be used to construct a metal-ion-based catalytic site similar to the natural one, using assembly methods found in photosynthesis. In a second approach, peptide-based water-soluble analogs of the natural photosynthetic oxygen-evolving complex will be sought. The DOE ALS in Berkeley will be used for X-ray (as necessary), XAFS and XANES characterization of the artificial water oxidation (and proton reduction) catalysts.

Hydrogen production catalysts will be based on natural hydrogenase enzymes. Iron-containing catalytic sites and iron-sulfur sites for storing reduction equivalents will be organized into functional catalysts using metal nanoparticles and linked to transparent electrodes.

New transparent, nanostructured, high-surface-area *conducting metal oxide* materials will be constructed to serve as functional frameworks for organizing the various components of the system, separating mutually reactive intermediates, and facilitating electrical communication among components.

A major challenge is the integration of the various components mentioned above into a functional system that is competent to carry out water splitting as a unit. This will require careful attention both to the thermodynamic and kinetic properties of the catalysts and charge-separation units and to the transport of redox equivalents and materials among the various units of the complex. Thus, the research has a strong *systems engineering* component. Two photosystems, à la photosynthesis, will likely be necessary to achieve useful efficiencies. Initially, metallic connections between some subsystems will be used in order to permit testing of components electrochemically and application of external electromotive force as necessary. Based on the performance of natural photosynthesis, the synthetic system has the potential to produce fuel efficiently from sunlight and water, to be inexpensive, to use earth-abundant elements, and to be a practical solution to humanity's energy problems. Realizing this potential is a significant fundamental and applied scientific challenge.

While pursuing this ambitious goal, the Center will uncover basic scientific knowledge that will point the way to new catalysts for water splitting and fuel cells, new materials for solar photovoltaics of various kinds, new ways to use DNA and peptides for preparation of artificial enzymes for biomedical and other technological applications, and new fundamental ways of understanding and manipulating matter that will have applications in many different areas of technology. It may also help identify ways to modify natural photosynthesis in plants so that it can better fill humanity's needs.

Center for Bio-Inspired Solar Fuel Production	
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Center for Interface Science: Solar Electric Materials
EFRC Director: Neal R. Armstrong
Lead Institution: University of Arizona

Mission Statement:

We will become a nationally and internationally recognized center of excellence for science of interfaces in photovoltaic devices based on organic and inorganic nanostructured hybrid materials. Our Center will inspire, recruit, and train future scientists and leaders in the basic interface science of solar electric energy conversion.

The Center for Interface Science: Solar Electric Materials will:

- Develop new theories to better understand charge transfer between organic semiconductors and oxides and metals and emerging non-traditional conductors.

- Develop new methodologies for the characterization of the atomic and molecular composition of interfaces, and new approaches to the nanoscale characterization of electrical properties of these interfaces, and rates of electron transfer across phase boundaries.

- Develop new nanostructured hybrid materials that will lead to the formation of chemically and physically robust interfaces, with full control of their composition, their molecular architecture, and their physical (electrical, optical, thermo-mechanical) properties.

- Apply our understanding of nanoscale organic/oxide, organic/metal and organic/organic interfaces to existing and future solar energy conversion photovoltaic platforms.

Key scientific questions to be addressed include:

- How is the rate of (heterogeneous) electron transfer across organic/oxide, organic/organic and organic/metal interfaces controlled by the composition and electronic properties of the contact materials?
- How does heterogeneity of electrical properties in organic, oxide, and metal films, at sub-micron length scales impact macroscopic device properties?
- How is electron transfer across an organic/oxide, an organic/organic, or an organic/metal interface influenced by the surface coverage, bonding, orientation, redox functionality and dipolar nature of surface modifiers?
- How is electron transfer across an organic/oxide, an organic/organic, or an organic/metal interface affected by nano-texturing of the interface?
- How can one predict the thermo-mechanical and electrical stability of interfaces from their chemical composition?

Tools available in CIS:SEM to address these issues:

- Photoemission spectroscopies (UPS/XPS) and surface vibrational spectroscopic characterization of oxide/metal/organic interfaces, both for atomic and molecular composition and frontier orbital energies – including two-photon photoemission spectroscopies and microscopy on sub-micron length scales and sub-picosecond time scales;
- Atomic force microscopy (AFM) and conducting tip atomic force microscopy (C-AFM) for detailed characterization of physical and electrical properties of the critical

interfaces in solar cell technologies, at sub-micron length scales. State-of-the art electron microscopy (FE-SEM/TEM) for characterization of interfacial texturing and electrical properties;

- Waveguide-based (absorbance and luminescence) spectroelectrochemical and a.c. impedance characterization of heterogeneous electron transfer rates for monolayer-tethered small molecules, polymers and semiconductor nanoparticles, as function of coverage and orientation;
- Theoretical descriptions of oxide, metal and hybrid materials and their interfaces with small molecules and polymers, addressing the effect of composition and orientation on electronic properties of these interfaces;
- A wide array of vacuum deposition and solution deposition capabilities for the formation of new oxide, metal and hybrid contact and encapsulation materials tailored to provide robust interfaces for all Generation III solar cells;
- Synthetic capabilities for the creation of new interface modifiers to control interface energies (wettability), work function, height of charge injection barriers, and nanoscale "wiring" of conducting polymers to oxide and metal contacts – targets include molecular modifiers which will also control the molecular architecture of the organic layers which form the photocurrent-generating active layers in Generation III solar cells;
- Device fabrication and characterization facilities for a variety of vacuum-deposited and solution processed Generation III solar cells, with full characterization of their optical, electrical, structural and thermomechanical properties.
- Device and module level physical models are available for the modeling of the current voltage characteristics and the power conversion efficiency as a function of area.
- Capabilities are available for photovoltaic device lifetime testing under controlled temperature and relative humidity conditions, and for the quantitative characterization of water vapor transmission rates for device encapsulation.

Center for Interface Science: Solar Electric Materials	
University of Arizona	**Neal R. Armstrong (Director, Arizona)** **Jeanne E. Pemberton** (Assoc. Director -- Surface Science/Theory), **S. Scott Saavedra** (Assoc. Director -- Operations), **Dominic McGrath**, **Jeff Pyun**, **Oliver Monti**, **Robert Norwood**, **Nasser Peyghambarian**
Georgia Institute of Technology	**Seth R. Marder** (Assoc. Director -- Materials), **Bernard Kippelen** (Assoc. Director -- Device Science), **Jean-Luc Brédas**, **Samuel Graham**
National Renewable Energy Laboratories (NREL)	**David Ginley** (Assoc. Director & DOE Liaison), **Dana Olson**, **Joseph Berry**
University of Washington	**David Ginger**, **Christine Luscombe**
Princeton University	**Antoine Kahn**

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Center for Emergent Superconductivity
EFRC Director: J. C. Séamus Davis
Lead Institution: Brookhaven National Laboratory

Mission Statement: To carry out fundamental research leading to higher temperature and higher critical current superconductivity with the potential for application to a superconducting power grid.

As U.S. electrical energy consumption continues to grow, the nation's electrical power transmission grid faces fundamental structural challenges of capacity, reliability and efficiency if it is to meet the needs of the 21st century. Electricity demand will grow by 50% in the US and by 100% globally by 2030, with nearly all of that growth in cities and suburbs where the overhead power lines and underground cables are already saturated. Power delivery and control solutions based on superconductors could solve these crises by using their demonstrated higher current carrying capacities over conventional cables, self healing fault current limiting capabilities, and substantial increases in efficiency. However, there remain many fundamental materials and physics challenges which must be addressed in order for superconductivity to have broad impact on the electrical grid.

The objective of the BNL/ANL/UIUC ***Center for Emergent Superconductivity*** (CES) is to explore fundamental research issues with the objective to overcome key barriers leading to the viable application of high temperature/high current superconductivity. This will be achieved by enabling the design of superconducting materials with optimal physical and critical properties for deployment of a 21th century superconducting power grid. Thus, the most profound challenge of CES is to understand the fundamental mechanisms of high-temperature and high-current superconductivity sufficiently so as to direct discovery of new or improved families of materials with higher critical temperatures and currents.

The Center brings together a group of PIs with strong records of accomplishment and demonstrated records of collaboration from three world-leading research institutions in correlated electron superconductivity: Brookhaven National Laboratory, Argonne National Laboratory and the University of Illinois at Urbana-Champaign. Through their Center interactions, the PIs bring a diversity of crosscutting experimental and theoretical tools to pursue three key research objectives: finding **new strongly correlated superconducting materials**, understanding the **mechanisms leading to high temperature superconductivity**, and **controlling vortex matter to raise the current carrying performance** of high temperature superconductors.

Center for Emergent Superconductivity (CES)	
Brookhaven National Lab.	**J. C. Seamus Davis (Director)**, Peter D. Johnson John M. Tranquada Cedomir Petrovic Alexei Tsvelik Ivan Bozovic
Argonne National Lab.	George Crabtree Mike Norman J.C. Campuzano Wai Kwok Alexei Koshelev
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Light Matter Interactions in Solar Energy Conversion
EFRC Director: Harry Atwater
Lead Institution: California Institute of Technology

Mission Statement: To tailor the morphology, complex dielectric structure, and electronic properties of matter so as to sculpt the flow of sunlight and heat, enabling light conversion to electrical and chemical energy with unprecedented efficiency.

The long-term goal of the "Light-Matter Interactions for Energy Conversion" Energy Frontier Research Center (LMI-EFRC) is to create a national resource for fundamental optical principles and phenomena relevant to solar energy conversion, and for design of the optical properties of materials and devices used for energy conversion. The LMI-EFRC features a team that spans the campuses of Caltech, Berkeley and Illinois, and creates a foundational partnership between scientific world leaders in optical properties of matter with internationally recognized experts in solar photovoltaic and photochemical energy conversion and innovators in the design and fabrication of novel electronic and photonic materials.

This group will work together to create new solar metamaterials and forge new scientific understanding of light-materials interactions that together enable a new class of photovoltaic and photoelectrochemical structures possessing the robust nature of biological energy conversion structures, but with efficiencies approaching the limits of optoelectronic energy conversion. Architectures for precise control of light-matter interaction will span dimensions ranging from the greater-than-wavelength scale to the subwavelength scale, which will necessitate fabrication of complex photonic nanostructures and light absorbers. The goals and topical focus of the LMI-EFRC is strongly resonant with the DOE scientific grand challenges addressing mastery of energy and information on the nanoscale to create new technologies with capabilities rivaling those of living things.

Initial Five-year Objectives

- Design of an optical system capable of visible and ultraviolet light generation from sunlight, using cooperative upconversion, to greatly enhance the efficiency of photovoltaic energy conversion and photoelectrochemical water splitting.
- Define the limits to absorption and spontaneous emission in metallodielectric materials, yielding principles for design of ultrathin photovoltaic cells with scaling of light absorbers to nanoscale dimensions, enabling advances in photovoltaic conversion efficiency and reduced material utilization.
- Establish fundamental transformation optics principles for light absorption and emission in complex metamaterial structures.
- Develop light-driven material synthesis processes which enable energy conversion materials to develop their own complex architectures in response to illumination conditions and tailor light absorption in dielectric materials with complex architectures.
- Communicate research results that have transformational scientific impact and communicate scientific methods and developments to policymakers, technologists and the public so as to maximize the societal impact of EFRC research.

Center Research Team and Scientific Organization

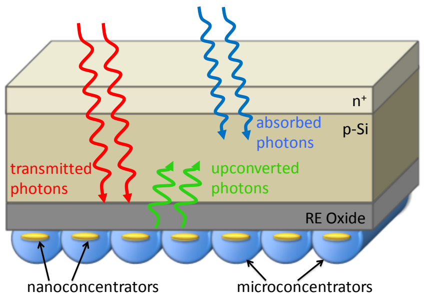

Figure 1. Photon upconversion process.

The faculty involved in the LMI-EFRC spans five academic departments (Applied Physics, Chemistry, Materials Science, Electrical Engineering and Mechanical Engineering) in the three institutions, Caltech, Berkeley and Illinois. The LMI-EFRC is organized scientifically into four Research Groups as follows:

The RG-1 "***Visible and Ultraviolet Generation by Upconversion***" team will develop materials and structures with the ability to control the optical properties of the resulting materials that enable efficient upconversion of the solar spectrum under little or no concentration. Such an approach would have very significant implications for both photovoltaic solar cell technology and solar fuel production. The ability to perform efficient upconversion would in many ways constitute a true paradigm shift in our ability to efficiently and cost-effectively produce electricity and fuels from sunlight.

The RG-2 team focused on "***Metal Optics for Spontaneous Emission and Absorption Enhancement***" will investigate plasonic phenomena that address the limits to absorption and spontaneous emission in dipole emitter and absorber materials coupled to metallic and metallodielectric structures

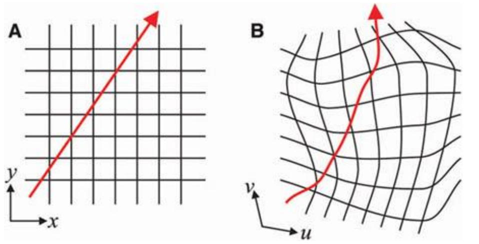

Figure 2. Principle of transformation optics. (a)light ray travelling in vacuum; (b) in coordinate-transformed medium.

The RG-3 team addresses"***Transformation Optics for Photovoltaics***" will take a new approach to photovoltaic absorber design using optical focusing by transformation optics. Transformation optics provides a novel way to control the propagation of light using metamaterials - ordered artificial structures with features smaller than the wavelength.

The RG-4 team "***Self-Architected and Complex Architecture Absorbers***" will develop photonic structures with preferential morphological and physical orientation of nanostructures on the macroscale. For example, photonic band gap structures require periodic 3-dimensional interpenetrating arrangements of absorbers and cavities that have different refractive indices. Photon management requires structures on the macroscale that have desired optical absorption, internal reflection, and light scattering properties. Solar cells based on nanostructures require preferential orientation of the materials to yield light absorption along a long axis that is preferentially oriented towards the source, and yet allow for orthogonal transport and collection of charge carriers in a three-dimensional network structure.

Light-Material Interactions for Energy Conversion (LMI-EFRC)	
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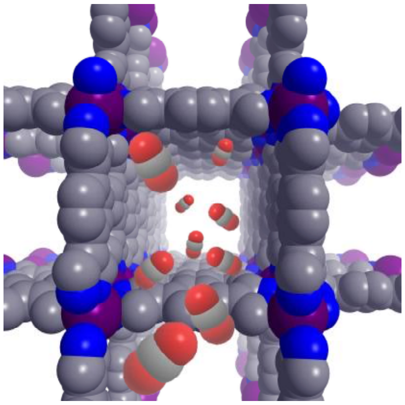
Center for Gas Separations Relevant to Clean Energy Technologies

EFRC Director: Berend Smit

Lead Institution: UC Berkeley

Mission Statement: the aim of this EFRC is to develop new strategies and materials that allow for energy efficient selective capture or separation of CO_2 from gas mixtures based on molecule-specific chemical interactions.

The separation of mixtures of volatile molecules presents a critical issue in the clean use of existing fuels and in the generation of alternative fuels. In particular separation of CO_2 is at present one of the mayor barriers for large scale CO_2 sequestration. For example, the conventional technology for capturing CO_2 from the effluent stream of a power plant may require as much as 25% of the electricity being produced. The EFRC will focuses on developing new strategies and materials for selective gas capture and separation based on molecule-specific chemical interactions.



The scientific challenge is to remove the fundamental scientific barriers that currently prohibit the efficient gas separations essential to the development of clean energy technologies. In gas separations these challenges are significant. The differences between the relevant gas molecules are small and therefore we need use the type of molecular control that is offered by nano science to tailor make materials that have exactly the right adsorption and diffusion selectivity to enable an economic separation process.

The center will combine personnel with expertise in the following areas of emphasis, with extensive overlap and interaction:

- *Materials Synthesis*: The synthesis of new gas-permeable materials with control over the molecular functionalities that have contact with gas molecules is deemed essential. Our focus here will be on: (i) generating metal-organic frameworks exhibiting high internal surface areas (up to 4,800 m2/g), and surfaces lined with robust and tailorable chemical groups, (ii) self-assembled polymer films with synthetic or biomimetic functional units.
- *Materials Characterization*: Detailed atomic-level structural characterization of the new materials will be necessary both before and after exposure to gas samples in order to probe hypotheses on interaction mechanisms. In addition, accurate means of assessing the selectivity, kinetics, and thermodynamics of gas adsorbate binding will be needed to demonstrate efficacy and test computational models.
- *Computational Separations*: A strong computational component to the research will be essential for understanding the chemical interactions at a molecular level, as well as for guiding the synthetic efforts toward materials exhibiting high specificity and tunable interaction energies.

We aim to develop fundamental new means of synthesizing materials with tailored molecular interactions, while generating new options for energy-related gas separations, including separation of CO_2 from power plant flue streams and separation of CO_2 from natural gas deposits.

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Texas A&M University	Hong Cai Zhou
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Molecularly Engineered Energy Materials (MEEM)
EFRC Director: Vidvuds Ozolins
Lead Institution: University of California, Los Angeles

Mission Statement: Create an interdisciplinary world-leading research center to design and synthesize revolutionary new materials for sustainable energy generation, storage and greenhouse gas capture based on cheap, abundant molecular building blocks; disseminate knowledge and increase societal awareness of sustainable energy issues through an integrated program of research, education, and outreach.

EFRC will focus on materials that are inherently inexpensive (such as polymers, oxides, metal-organic frameworks), can be easily assembled from intelligently designed building blocks (molecules, nanoparticles, polymers), and have the potential to deliver transformative economic benefits in comparison with the current crystalline- and polycrystalline-based energy technologies. We will conduct systematic studies of the fundamental mechanisms of carrier generation, energy conversion, as well as transport and storage of charge and mass in tunable, architectonically complex materials. Fundamental understanding of these processes will enable rational design, efficient synthesis and effective deployment of novel three-dimensional material architectures for energy applications. Three interrelated research directions where these novel architectures hold great promise for high-reward research have been identified: solar energy generation, electrochemical energy storage, and greenhouse gas capture.

Organic solar cells: We will design and synthesize novel molecules and nanoscale architectures (see e.g. Fig. 1) that can achieve or surpass 10% efficiency goal for organic solar cells. We will learn to control the nanometer-scale structure of conjugated polymers and polymer blends through the synthesis of novel materials and the use self-assembly techniques, with the goal of producing optimal nanometer-scale structures for photovoltaic applications. Another major goal is to understand how the nanometer-scale structure of conjugated polymer blends controls charge separation, carrier transport, carrier recombination and carrier extraction at the electrodes in working solar cells from both experimental and theoretical perspectives.

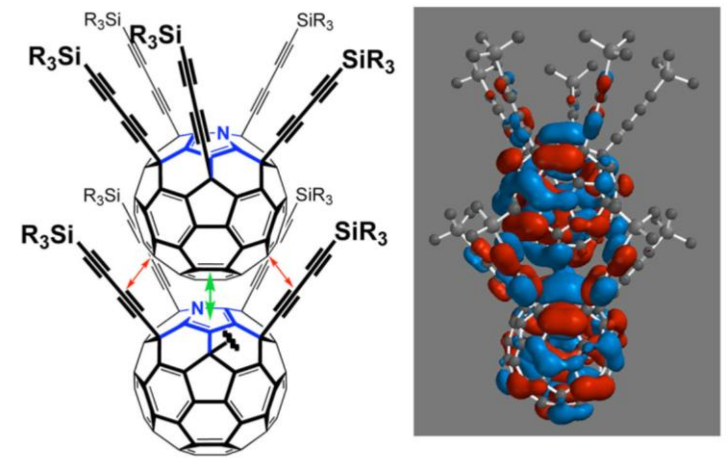

Figure 1. So-called "shuttlecock" molecules based on the heterofullerene $C_{59}N$ with phenyl "feathers" optimized for ideal close contacts within stacks. These molecules are expected to self-assemble into one-dimensional wires, enhancing the efficiency of charge separation and carrier transport in organic solar cells.

Electrochemical supercapacitors: Fundamentally, we will focus on determining why capacitive storage from metal oxides is much less than theoretical estimates; our working hypothesis is that inefficient charge transport in bulk insulating materials is a crucial bottleneck. We will design hierarchically structured electrode materials that integrate electronic and ionic conduction with pseudocapacitive charge storage. We will also search for new inexpensive materials that combine metallic conductivity with ability for capacitive store charge and explore the efficiency of capacitive charge storage in nanoporous materials using both theoretical and experimental approaches.

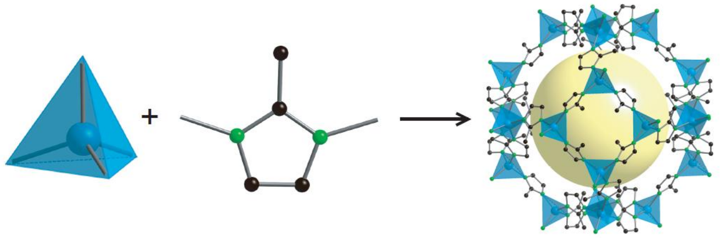

Figure 2: Schematic representation of ZIF formation (ZIF-8, right). ZnN_4 tetrahedra are blue, C, and N atoms are black and green spheres. H atoms are omitted for clarity. The yellow sphere represents the largest sphere that occupies the cavity without contacting the interior van der Waals surface. These materials have been shown to selectively absorb carbon dioxide and other greenhouse gases.

Capturing greenhouse gases: A coordinated effort is proposed for the high-throughput synthesis, characterization and modeling of zeolitic imidazolate frameworks (ZIFs). The structures of ZIFs consist of imidazole groups connected by organic linkers (see Fig. 2) and feature high porosity (2000 m^2/g), high thermal stability (500 °C), and unusually high chemical stability. They have been shown to selectively absorb carbon dioxide and other greenhouse gases. Our research will elucidate the correlation between the structure of a ZIF and its performance, identify the adsorptive sites within the pores of ZIFs, and develop strategies for optimizing the performance of ZIFs to affect highly selective carbon separation.

The three research trusts will be integrated on the basis of common scientific challenges at the fundamental level of electrons, atoms, and molecules: creating innovative nanometer-scale material architectures from custom-designed molecular building blocks to achieve fast, highly efficient charge and mass transfer, and specifically tailored thermodynamics of charge and mass storage.

Molecularly Engineered Energy Materials (MEEM)	
University of California, Los Angeles	**V. Ozolins (Director)**, B. N. Dunn (Assistant Director), Y. Lu**,** D. Neuhauser**,** L. Pilon**,** Y. Rubin**,** B. J. Schwartz**,** S. H. Tolbert**,** O. M. Yaghi
University of California at Davis	M. D. Asta
University of Kansas	B. Laird
National Renewable Energy Laboratory	N. Kopidakis
Eastern Washington University	Y. Hondonougbo

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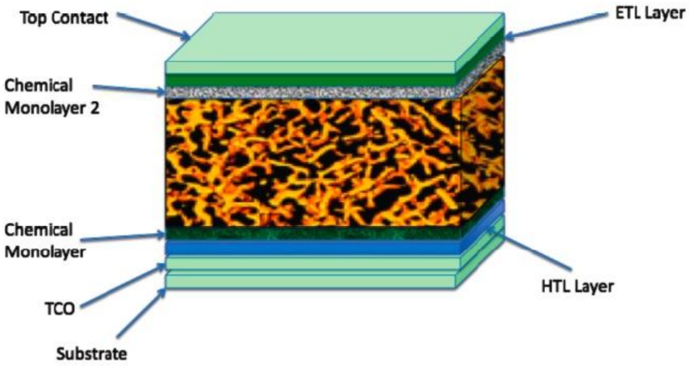
Center for Energy Efficient Materials (CEEM)
EFRC Director: John Bowers
Lead Institution: University of California, Santa Barbara

Mission Statement: To provide a critically important part of the solution to the broader energy crisis through focusing on fundamental research in novel materials for photovoltaics, thermoelectric waste heat recovery, and solid-state lighting.

As a result of the energy crisis facing the United States, the scientific enterprise must offer solutions, based on fundamental research and engineering, that will ensure sustainable energy resources for the US over the long term. The Center for Energy Efficient Materials (CEEM) addresses this critical challenge by focusing on fundamental research in the three key areas of photovoltaics, thermoelectrics, and solid state lighting. While the world's growing energy needs cannot be fully addressed by any one center, the successful outcome of the proposed research will provide a critically important part to the full solution.

Photovoltaics

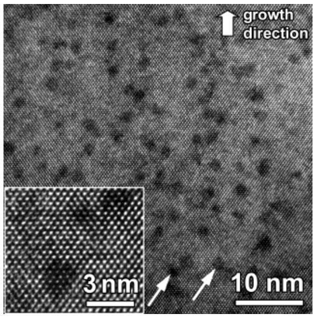
CEEM will take a comprehensive, integrated approach to dramatic improvement in photovoltaic technology, anticipating lower cost manufacturability with organic solar cells, higher performance epitaxial photovoltaics for concentrated PV and truly novel materials and device structures in the longer timeframe that will address both higher efficiency and lower cost:



1. Organic ("plastic") cells hold the promise of low cost and large area manufacturability. Controlled nano-scale phase separation enables formation of "bulk heterojunctions" to achieve nearly 100% separation of electrons and holes in the organic film, with subsequent charge collection at the electrodes. By synthesis of new materials with improved coverage of the solar spectrum, by implementing these new materials in tandem cell architectures, and by tuning band energies to optimize the open circuit voltages, efficiencies in excess of 15% are possible.
2. The highest efficiency PVs have been reported for multi-junction solar cells, but these still do not span the full solar spectral range. We will investigate incorporating the (In,Al,Ga)N family of materials in PV applications since these materials together do span the full solar spectral range and offer the possibility for even higher efficiency for PVs with multiple absorbing regions. Additional materials combined with metamorphic growth and bonding offer additional ways to improve efficiency.
3. Novel Nanostructured and Bio-inspired Photovoltaic Materials: Dramatic improvements in PV operation, bringing performance much closer to the thermodynamic limit, may arise from the ability to create truly 3-dimensional device structures from nanoscale components, allowing control of critical length scales that determine the efficiency of not only photon absorption, but also of carrier separation and collection. We will pursue techniques that are templated by both organic nanostructures and natural, biological templates with engineered specificity for inorganic building blocks. Bio-inspired, as well as bio-templated PV materials promise low-temperature and low cost synthesis of novel nanostructured inorganic PV thin films. The utilization of environmentally-benign synthetic conditions represents a long-term route to dramatically reduced cost.

Thermoelectrics

New thermoelectric materials with higher efficiencies are critically important for power generation and waste heat recovery. Material breakthroughs would allow a variety of new applications, such as an attractive compact alternative to internal combustion engines and solid state refrigerators. We are proposing a variety of metal/semiconductor nanocomposites that will allow us to modify the three intrinsic material properties important for high efficiency. The key is growth of these novel materials and structures, which are largely unexplored. Three approaches for growing thermoelectrics will be pursued, MBE, CBE, and MOCVD for precise control of material compositions, followed by bulk and chemistry approaches to synthesize these materials in volume at low cost. We are looking at segmented approaches to combine thermoelectric elements in series to optimize each material in its temperature range. We will focus on utilizing our expertise in nanostructure design and synthesis, the incorporation of nanostructures into prototypical devices, and the knowledge gained by studies of the basic physics and properties of thermoelectric materials to develop synthetic chemical methodologies for producing practical, large-area thermoelectric arrays that have the potential for commercial use.



Solid State Lighting

While current solid-state lighting devices show quite good efficiencies at both ends of the visible range, there is a dramatic drop in the yellow-green region. We believe that part of the droop should be controlled thanks to the non polar growth as one part of it has been identified as due to increased carrier leakage induced by the QCSE, and another part to Auger effect, more tentatively so far but supported by our preliminary theoretical efforts. Both effects are to be massively reduced with non polar material, the former due to the absence of polarization fields, the latter due to the use of wide QWs or even DHs. We will carry out systematic experiments to identify the other origins of the droop. Today's limits on GaN device performance are in large part due to insufficient basic knowledge of these rather recent materials. Better understanding has to be gained to identify the better long term solutions to today's limits. Also, newer device concepts and growth techniques have to be explored to surpass present implementations.

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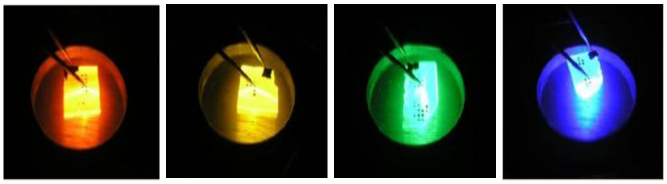

Center for Energy Efficient Materials (CEEM)	
University of California, Santa Barbara	J. Bowers (Director), A.J. Heeger , F. Wudl, G. Bazan, G. Stucky, A. Gossard, S. Nakamura, S.P. DenBaars, J. Speck, C. Van de Walle, E. Hu, T.Q. Nguyen, U.K. Mishra, D. Morse, M. Moskovits, C. Weisbuch, C. Palmstrom, J.M. Tarascon, M. Chabinyc
National Renewable Energy Laboratory	D. Friedman, D. Ginley, A. Ptak
Los Alamos National Laboratory	D. Smith
University of California, Santa Cruz	A. Shakouri
Harvard	E. Hu

Center for Energy Frontier Research in Extreme Environments (EFree)
EFRC Director: Ho-kwang Mao
Lead Institution: Carnegie Institution

Mission Statement: Efree focuses on accelerated discoveries of novel materials and phenomena in the extreme pressure-temperature environments and recoveries of the favorable properties for energy applications under ambient conditions.

High pressure categorically alters materials behavior, including phonon, electronic, magnetic, structural, and chemical properties, including bonding, reactivity, and kinetics. Pressure pushes materials across barriers between insulator and superconductor, fluid and solid, molecular and extended frameworks, and the vigorously reactive and the inert. Extreme *P-T* studies provide a new route towards discovering new materials with enhanced performance for a broad range of applications from energy transformation (*i.e.* solar, mechanical, chemical to electrical), energy storage (*i.e.*, batteries, capacitors, hydrogen), energy transmission, sensing and monitoring, to advanced structural materials. In the pressure dimension, creation of novel materials and observation of novel phenomena become the rule rather than exception.

Efree organizes a team of leading scientists with complementary expertise in high-pressure science and technology, theory and experimentation, physics, chemistry, geoscience, and materials science. Efree will develop the critical, enabling technologies at national facilities and Carnegie Institution, including the next-generation high *P-T* devices and the integration of extreme environments with synchrotron x-ray, neutron, laser, optical, electronic, magnetic, and nano-scale probes. With this comprehensive platform, we can anticipate major discoveries and breakthroughs in four thrust areas.

1. Novel Superconducting, Electronics, and Magnetic Materials Under Extreme P-T – Pressure is opening up broad new vistas on superconductivity from simple elements to complex materials and the creation of new electronic and magnetic materials of great significance to energy science. Emergent properties of correlated electron materials include ferromagnetism, antiferromagnetism, unconventional and high-temperature superconductivity, charge- and orbital-density waves, electronic phase separation, stripes, ferroelectricity, colossal magneto-resistance and magneto-capacitance. Correlated materials, such as high T_c superconductors, spintronic materials, Mott insulators, colossal magneto-resistivity materials, spin Peierls materials, heavy fermion materials, and quasi low-dimensional materials, could be greatly superior to conventional materials for problems ranging from efficient charge injection in photovoltaic devices to lossless electrical transmission over superconducting lines.

2. Novel Hydrogen and Hydrogen-Bearing Systems Under Extreme P-T – The interest in hydrogen now extends well beyond the elemental forms to encompass hydrogen-containing molecular alloys and compounds for hydrogen storage applications. EFree will conduct a broad-based program of research that includes work on the elemental states and those with hydrogen in chemical compounds, where results in one area will inform work in the other.

3. Novel Light-Element and Covalent Materials Under Extreme P-T – Light elements and their compounds form widely-used energy materials with unique properties such as superconductors, diamond and cBN, and tough lightweight carbon-based materials. We will apply variable high-*P*, *T* and strain rate to synthesize new materials and/or to study their response. The experimental results obtained will lead to discovery of new phenomena under extreme conditions and, by working in a close connection with EFree theorists, will allow us to develop a better understanding of the materials behavior for future energy technologies.

4. Novel Nanophase, Composite, Amorphous and Geological Materials Under Extreme P-T – Nanophase and composite materials exhibit enhanced performance that complements bulk crystalline materials over a broad range of high *P-T* conditions. These materials have potential for future applications in energy efficiency, production, and storage. EFree will address the underlying origin of transitions from crystalline to amorphous materials.

To recover the novel high-pressure materials metastably at ambient pressure far away from equilibrium is central to the EFree approach. Mounting examples reveal that the combination of high pressures and low temperatures not only *brings* matter, but also *sustains* matter, very far away from equilibrium. The combination of *P-T* conditions with extreme radiations is uncovering new phenomena and materials. In these studies, pressure provides a powerful means for continuously tuning the free energy of the system; x-ray photons excite systems into highly metastable states, and low temperature and chemical tuning prevent the system from reaching equilibrium. By varying these parameters, characterizing the dynamically compressed or stressed and electronically excited materials with time-resolved probes, and combining these efforts with first-principles calculations, transition mechanisms and energy landscapes can be revealed. Such knowledge is essential for the recovery of materials to ambient conditions for use in numerous energy applications.

Center for Energy Frontier Research in Extreme Environments (EFree)	
Carnegie Institution	**H.K. Mao (Director)**, **R.J. Hemley (Associate Director)**, R. Boehler, G.D. Cody, R.E. Cohen, Y. Fei, A.F. Goncharov, G. Shen, V.V. Struzhkin
Arizona State University	J.L. Yarger, E. Soignard
California Inst. Tech.	B. Fultz
Cornell University	N.W. Ashcroft, R. Hoffmann
Florida International U.	J. Chen
Missouri State U.	R.A. Mayanovic
Penn State University	J.V. Badding
Stanford University	W.L. Mao
U. of Texas at Austin	J. Lin
Argonne National Lab.	M. Guthrie, G.G. Long, G. Srajer
Brookhaven Nat. Lab.	Y. Cai, C. Kao
Jefferson Nat. Lab.	G.P Willams
L. Livermore Nat. Lab.	J.C. Crowhurst, M.R. Armstrong, E.J. Reed
Los Alamos Nat. Lab.	Y. Zhoa
Oak Ridge Nat. Lab.	C.A. Tulk

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Re-Defining Photovoltaic Efficiency Through Molecule Scale Control

EFRC Managing Director: James Yardley

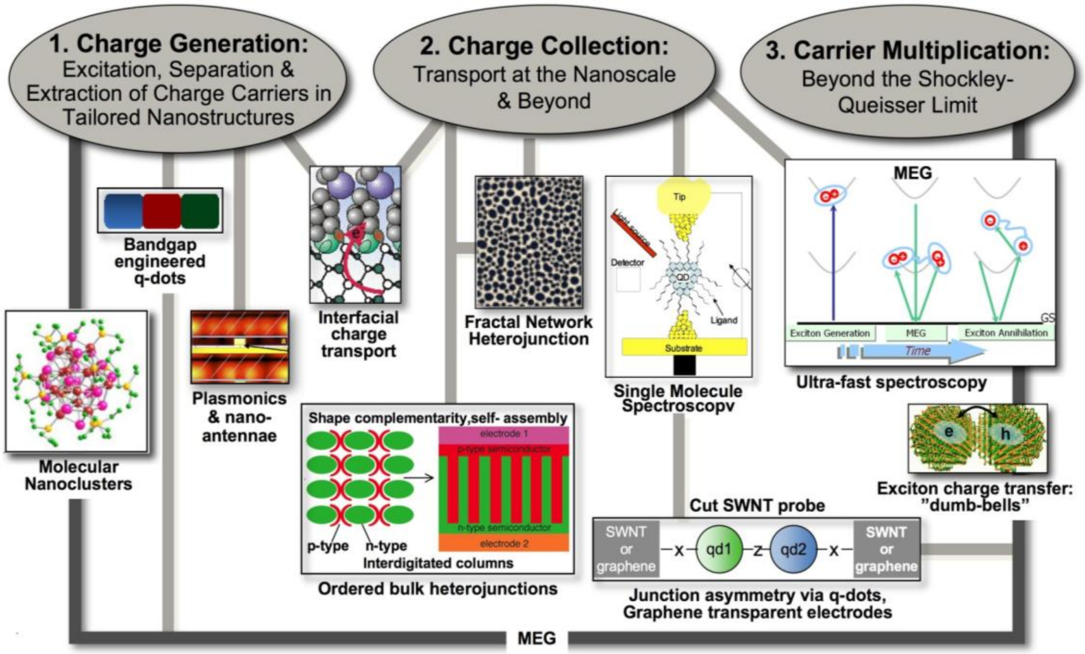
EFRC Scientific Directors: Louis Brus and Tony Heinz

Lead Institution: Columbia University

Mission Statement: The ultimate goal of the Columbia EFRC is to create enabling technology which will redefine photovoltaic efficiency through fundamental understanding and molecule-scale control of the key steps in the photovoltaic process in organic and hybrid materials.

The primary approach of the EFRC is to develop new fundamental understanding that will enable the development of revolutionary highly-efficient inexpensive photovoltaic solar cells. The EFRC will focus its expertise in chemical synthesis, fabrication, manipulation, and characterization of nanoscale materials and materials theory in order to: (1) systematically develop the fundamental understanding of the primary photovoltaic processes in organic and hybrid materials needed to advance inexpensive solar cells to reach the well-known Shockley-Queisser efficiency limit; and (2) develop and quantitatively investigate new nanostructured materials with potential for extracting multiple electrical charges from a single absorption event thus establishing a scientific basis for moving the efficiency of these solar cell devices well beyond the Shockley-Queisser efficiency limit. The new understanding and novel nanomaterials developed by this research team will play a key role in enabling the development highly-efficient solar energy technologies. The research program of the EFRC centers around three multi-site, multi-disciplinary, and interlocking research thrusts. Each thrust represents an integrated effort incorporating theory, materials, and measurement.

Schematic of Columbia University EFRC Research Program.



Thrust 1 is dedicated to "Charge Generation: Excitation, Separation, and Extraction of Charge Carriers in Tailored Nanostructures." In this thrust we are developing a set of new, chemically well-characterized nanoscale materials. These include new quantum dots including asymmetric quantum dots and a set of novel chemical compounds that we call "molecular clusters." We are quantifying the dynamics and effectiveness of fundamental processes, using modern nanoscience tools including ultrafast and single molecule spectroscopies. We are also building a theoretical framework to model kinetic processes of charge transport, with input from atomic scale calculation of local bonding, structure, and electronic states. We are measuring the effectiveness of charge transport across interfaces using a variety of techniques including photoemission.

Thrust 2 examines aspects of "Charge Collection: Transport at the Nanoscale and Beyond." In this thrust we build new materials suitable for studying the fundamental physics in bulk heterojunction solar cell devices including new chemically-tailored semiconductor materials and ordered interfaces. We are developing theoretical models for exciton dissociation, diffusion, and separation in these structures. We support these models with nanofabricated devices using both top-down and bottom-up approaches. We directly measure charge transport in these systems.

Thrust 3 explores "Carrier Multiplication: Beyond the Shockley-Queisser Limit." Our program is first working to identify clear experimental signatures for multi-exciton generation (MEG) and related singlet fission processes for producing multiple charge carriers. We are developing structures and materials for optimal carrier multiplication schemes including MEG. This involves systematic exploration of MEG and related phenomena in quantum dot and carbon-based systems such as graphene nanoribbons or carbon nanotubes using direct charge carrier detection as well as a variety of spectroscopic techniques. Finally this thrust seeks to establish quantitative and predictive theory for MEG and related carrier multiplication concepts.

Center for Re-Defining Photovoltaic Efficiency Through Molecule Scale Control	
Columbia University	**James Yardley (Managing Director)**, **Louis Brus (Scientific Director),** **Tony Heinz (Scientific Director)**, Simon Billinge, George Flynn, Irving Herman, James Hone, Philip Kim, Ioannis Kymissis, Colin Nuckolls, Richard Osgood, David Reichman, Kenneth Shepard, Michael Steigerwald, Latha Venkataraman, Chee Wei Wong
University of Arkansas	Xiaogang Peng
Purdue University	Ashraf Alam
University of Texas	Xiaoyang Zhu
Brookhaven National Laboratories	Charles Black, Mark Hybertsen

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Energy Materials Center at Cornell (EMC^2)
EFRC Director: Héctor D. Abruña
Lead Institution: Cornell University

Mission Statement: The basic aim of this EFRC is to achieve a detailed understanding, via a combination of materials synthesis, experimental and computational approaches, of how the nature, structure, and dynamics of nanostructured interfaces affect energy generation, conversion and storage with emphasis on fuel cells and batteries.

Few aspects are as pervasive and important in energy generation, conversion and storage as the nature and structure of interfaces. Reactions at electrodes in fuel cells, charging and discharging reactions in lithium ion batteries and supercapacitors, and numerous catalytic systems all depend critically on the nature and structure of interfaces between materials and/or different states of matter. Despite their fundamental importance and evident technological relevance, our understanding of these processes is, at best, rudimentary. This is due, at least in part, to the lack of well-defined systems, both experimental and computational, as well as techniques that can provide structural and compositional information *in-situ* and under realistic operating conditions. This is especially true for systems that normally operate far from equilibrium.

We propose an EFRC whose overriding theme will be the understanding the nature, structure, and dynamics of these interfaces on energy generation, conversion and storage with emphasis on fuel cells (Fig. 1A) and batteries (Fig. 1B). The center will integrate the synthesis of model systems (Figure 1 C, E) with atomic level control (Fig. 1I) along with combinatorial libraries (Fig. 1F and G), and computationally characterize these materials (Fig. 1D). These efforts will guide the synthesis of improved materials and the development of tools (Fig. 1 H and I) that will provide *in-situ* spatiotemporal characterization over the range of conditions in which the appropriate technologies are intended to operate.

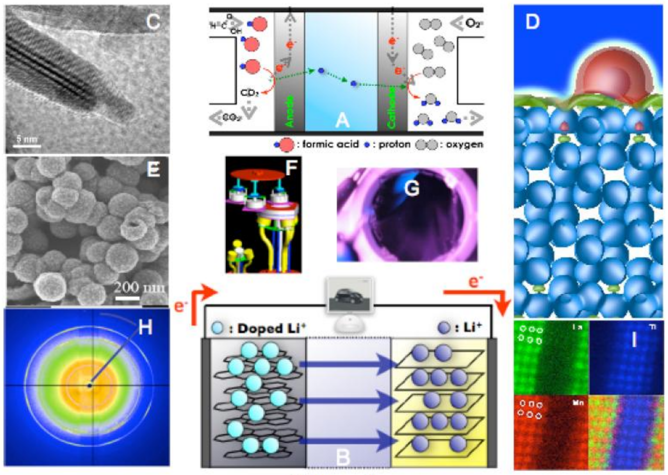

Figure 1

The proposed studies are aimed at greatly accelerating the development of energy conversion technologies by providing the fundamental knowledge-base for the rational development and synthesis of new materials, as well as experimental and computational tools necessary for and critical to optimization of properties and, thus, performance.

The fundamental challenges that we will address include:

- Achieve a microscopic understanding of the effects of the nature and structure of nano-structured interfaces between dissimilar materials including metal/conducting polymer, and at “atomically engineered” complex oxides on energy generation, conversion and storage
- Develop and apply novel experimental tools for probing the dynamics and kinetics of structure and chemistry at interfaces, in films and in model devices

- Develop and employ computational and modeling platforms to understand the fundamentals underlying the above phenomena

Potential Impact:
These investigations will dramatically accelerate the development of energy generation, conversion and storage technologies with emphasis on fuel cells and batteries and thus, the evolution of the entire energy landscape.

Energy Materials Center at Cornell (EMC^2)	
Cornell University	**Director:** H. D. Abruña **Thurst Groups Leaders:** L. A. Archer, J. D. Brock, F. J. DiSalvo, D. A. Muller **Participating Faculty:** T. Arias, G. W. Coates, J. Engstrom, C. Fennie, E. Giannelis, T. Hanrath, R. Hennig, J. Marohn, R. Robinson, D. Schlom, R. B. VanDover, U. Wiesner
Lawrence Berkeley National Lab.	J. Neaton

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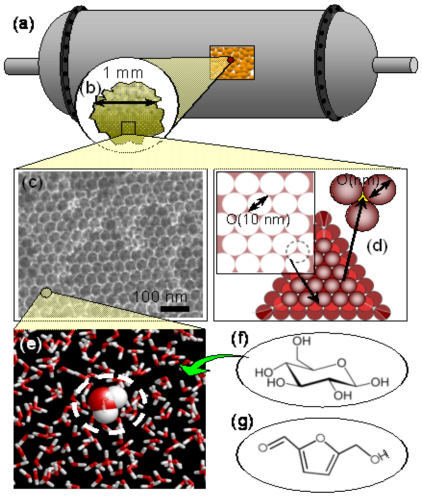
Catalysis Center for Energy Innovation (CCEI)
EFRC Director: (Dion Vlachos)
Lead Institution: (University of Delaware)

Mission Statement: Develop innovative heterogeneous catalytic technologies for future biorefineries and educate the workforce needed to lead to further, sustainable economic growth of the US.

The Catalysis Center for Energy Innovation (CCEI) aims at developing innovative, science-based heterogeneous catalytic technologies for transformation of biomass materials into fuels, chemicals, and electricity. Biomass offers a unique opportunity for a sustainable society with unprecedented impact on the US economy, energy security and independence. For this vision to be realized, major scientific hurdles need to be overcome due to the inherent complexity of biomass materials and associated processes. Reactions typically take place in a complex, multiscale environment that renders the rational design of these processes and catalysts very challenging.

The overall objectives of the CCEI-EFRC are to develop the enabling science that can eventually lead to viable, economic operation of biorefinery technologies from various biomass feedstocks and to educate the workforce needed for these new positions that can lead to further, sustainable economic growth of the US.

Since biomass feedstocks vary considerably with source, and the number of candidate reactions is huge, the CCEI will mainly focus on developing a fundamental science base for controlling the scission and formation of C-H, O-H, C-C and C-O bonds by choosing a select number of reactions from a representative group of processes. Our overarching goal is that the methods and concepts developed herein could form the foundations of modern biorefineries. The cornerstone of the CCEI lies in advancing catalysis and electrocatalysis and integrating them with reactors into processes in order to deliver innovative technologies for the conversion of feedstocks of cellulose, sugars, produced, e.g., from the hydrolysis of biomass, and smaller polyols. We have assembled an interdisciplinary team of faculty that brings together the necessary expertise and synergism to tackle this – at first glance – insurmountable problem.



We plan to exploit three complementary catalytic technological platforms anticipated to play key roles in biorefineries and energy/chemical production: Non-aqueous phase processing to produce fuels, aqueous phase processing to selectively produce chemicals, and direct conversion of biomass derivatives to electricity using novel direct carbon fuel cells.

In order to overcome the scientific barriers arising from handling these feedstocks, the CCEI will develop three crosscutting research thrusts, namely multiscale modeling to handle the inherent complexity of the environment in which reactions take place, hierarchical multiscale materials that are hydrothermally stable, possess tunable porosity with bio-inspired functionality grafted, and minimize molecular traffic resistance while allowing shape selectivity, and cutting-edge characterization methods to probe reactions often under in situ environment. Research at the Brookhaven National Laboratories will be central for in situ catalyst characterization of the CCEI.

The CCEI outcomes will include a fundamental understanding of the reaction mechanisms of representative biomass thermochemical transformations, a rational framework for multiscale hierarchical catalytic materials and process design, science-based innovative technologies for biomass utilization, education of students and postdocs, and effective outreach/dissemination pathways to other scientists and the public.

Catalysis Center for Energy Innovation (CCEI)	
University of Delaware	**D. G. Vlachos (Director)**, J. G. Chen, R. F. Lobo, M. A. Barteau, J.A. Lauterbach, D. J. Buttrey, D. J. Doren, S. I. Sandler, K.H. Lee
University of Pennsylvania	R. J. Gorte and J. M. Vohs
Lehigh University	M. A. Snyder
University of Massachusetts, Amherst	S. M. Auerbach, G. W. Huber
University of Minnesota	M. Tsapatsis, A. Bhan
California Institute of Technology	M. E. Davis
University of Southern California	H. Wang

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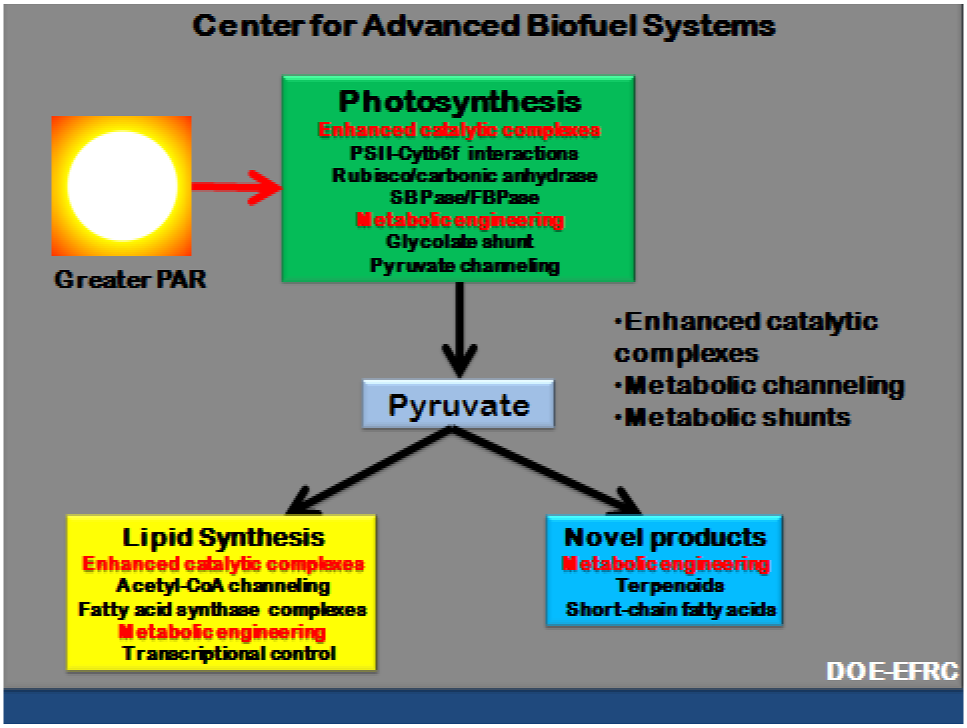
Center for Advanced Biofuel Systems
Richard T. Sayre, Director
Donald Danforth Plant Science Center

The broad objectives of the Center for Advanced Biofuel Systems are to increase the efficiency of select plant- and algal-based reduced carbon (oil and specialty fuel) production systems using rational metabolic engineering approaches grounded in modern systems biology.

Our strategy is to develop integrated and optimized metabolic flux networks that increase the efficiency of solar energy conversion into oils and other biofuel components. This will be achieved by: 1) employing novel protein catalysts that increase the thermodynamic and kinetic efficiencies of photosynthesis and oil production, 2) engineering metabolic networks to enhance acetyl-CoA production and channeling towards neutral lipid synthesis, and 3) engineering new metabolic networks for the production of hydrocarbons required to meet commercial fuel standards. These strategies will be informed by comprehensive metabolic flux analyses of select algal and crop systems and computational modeling that will direct strategies for enhanced biofuel production. What distinguishes our approach from many others is that we integrate all aspects of metabolism, from light capture in photosynthesis through end product production.



Center for Advanced Biofuel Systems

Greater PAR

Photosynthesis
Enhanced catalytic complexes
PSII-Cytb6f interactions
Rubisco/carbonic anhydrase
SBPase/FBPase
Metabolic engineering
Glycolate shunt
Pyruvate channeling

Pyruvate

- Enhanced catalytic complexes
- Metabolic channeling
- Metabolic shunts

Lipid Synthesis
Enhanced catalytic complexes
Acetyl-CoA channeling
Fatty acid synthase complexes
Metabolic engineering
Transcriptional control

Novel products
Metabolic engineering
Terpenoids
Short-chain fatty acids

DOE-EFRC

The technologies our investigators will employ to address these objectives include:

> 1) Development of computation tools and metabolic flux models to direct engineering strategies that enhance biofuel production. Drs. Leslie Hicks, Yair Schachar-Hill and David Gang will work coordinately with each of the other co-PIs to develop these tools and models.

2) Development and introduction of catalytically enhanced or multi-functional enzyme complexes to increase the thermodynamic and kinetic efficiencies of biofuel production, including assembly of novel macromolecular catalytic complexes that reduce diffusion or enhance catalytically rate-limiting processes to channel metabolic flux. Drs. Sayre, Kutchan, Jaworski and Yu will develop new enzyme complexes that reduce bottlenecks and introduce novel metabolic pathways to channel reducing equivalents generated from the photosynthetic light reactions through the Calvin cycle ultimately to oil production.

3) Identification and manipulation of metabolic and/or transcriptional control elements that regulate the expression of targeted metabolic pathways focusing on the central role of acetyl-CoA in oil production. Drs. Wang and Yu will characterize and manipulate

4) Generation of short- and medium-chain fatty acids and novel biofuel products (aromatic hydrocarbons) to meet fuel standards (e.g. JP8) using photosynthetic organisms. Drs. Cahoon, Jaworski, Wang, Yu and Sayre will work coordinately to manipulate metabolic flux channeling to increase the yields of biofuel products.

5) Dr. Terry Woodford-Thomas will direct our outreach and educational activities.

Center for Advanced Biofuel Systems (CABS)		
Institution	**Investigator**	**Contact information**
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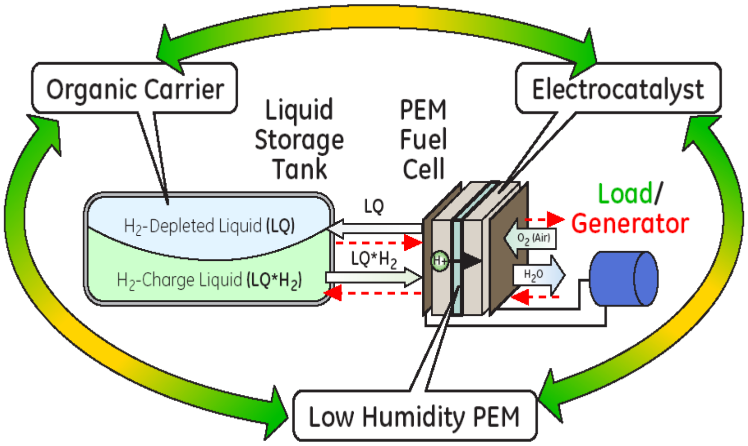
Center for Electrocatalysis, Transport Phenomena, and Materials (EFRC-ETM) for Innovative Energy Storage

EFRC Director: Dr. Grigorii Soloveichik

Lead Institution: General Electric Global Research

Mission Statement: *Develop the fundamental basis for an entirely new high-density energy storage system that combines the best properties of a fuel cell and a flow battery.*

The basis of the organic fuel cell/flow battery system concept is a simple idea: instead of common approach of dehydrogenating an organic liquid carrier in a catalytic reactor to generate hydrogen gas and feed it to a hydrogen-air PEM fuel cell, the CETM proposes to feed the hydrogenated organic liquid carrier directly into the fuel cell where it will be electrochemically dehydrogenated to a stable, hydrogen depleted organic compound without ever generating $H_{2.}$ As with normal hydrogen-air fuel cells, this new system will reduce oxygen from air at the cathode. The spent organic carrier may be replenished either by mechanical replacing with the fresh hydrogenated carrier at a refueling station or by electrochemically charging using protons from water electrooxidation.



The CETM has identified three major research thrusts in electrocatalysis transport phenomena in membranes, and materials to make this concept a reality. The selection of organic carriers suitable for organic fuel cell/flow battery will be based on thermodynamic and kinetic factors central to hydrogenation and reversible dehydrogenation reaction mechanisms and will be assisted by computational modeling.

Understanding of the electrodehydrogenation and electrohydrogenation catalysis is critical for realization of the organic fuel cell/flow battery concept. A good electro(de)hydrogenation catalyst should combine an effective (de) hydrogenation activity with an ability to mediate transport of protons and electrons. Because only a few examples of catalysts for electrohydrogenation and electrodehydrogenation of organic heterocycles are known, catalyst leads from among the following classes of catalyst will be explored: i) catalysts for electrohydrogenation of $CO_{2,}$ catalysts for hydrogenation of arenes, particularly heteroarenes, iii) catalysts for hydrogenation of imines, iv) catalyst for activation of the C-H bonds, and v) catalysts that can reduce water to H_2. The emphasis will be made on the non-precious metal complexes and materials.

Various strategies will be explored for attaching electrodehydrogenation/ hydrogenation catalysts to electrode materials with an emphasis on chemically robust attachments and rapid transfer of electrons and protons between the electrode and the catalyst. The coverage of the catalyst on the surface of the electrode material, its electron storage capacity and electron transfer between the electrode and the catalyst of the catalyst will be studied to identify any limitations placed on the electrodehydrogenation and electrohydrogenation activities.

To develop a novel proton exchange membrane, it is necessary to study the transport phenomena in the bulk material as a separator and the material properties needed to facilitate the convergence of charge and molecular transport to the site of the catalysis and the equally rapid removal of the products. Four major problems will be investigated: plasticizing of polymers with the organic carriers, replacement of water with other proton conductive phase, morphology control, and effect of polymer structure on membrane properties.

Since all three components of the proposed organic fuel cell/flow battery should work together seamlessly, the special emphasis will be made on fundamentals of 3-D three-phase interface including electrically conductive component, ion-conductive ionomer, and the electrocatalyst to ensure good transport of organic carrier in both hydrogenated and dehydrogenated forms, protons and electrons.

Center for Electrocatalysis, Transport Phenomena, and Materials (EFRC-ETM) for Innovative Energy Storage	
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Yale University	R.H. Crabtree, V.S. Batista
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Center for Materials Science of Nuclear Fuel
EFRC Director: Dieter Wolf
Lead Institution: Idaho National Laboratory

Mission Statement**:** to develop an experimentally validated multi-scale computational capability for the predictive understanding of the microstructure dynamics and its impact on thermal transport in nuclear fuel under irradiation with application to UO_2 as a model system.

Project Description: The goal of the *Center for Materials Science for Nuclear Fuel* is to develop a predictive multi-scale modeling framework that captures how defect generation and evolution and microstructure changes under irradiation lead to the degradation of fission-reactor fuel properties. Degradation of the thermo-mechanical behavior results from the cumulative, intricately coupled effects of fission-damage processes, high temperatures and high thermal gradients. Yet, apart from large empirical databases, a fundamental predictive science basis that connects “structure” across the relevant length and time scales with fuel behavior does not currently exist. To elucidate the underlying point-defect and microstructural mechanisms controlling this degradation behavior, we will develop a predictive computational framework based upon the non-linear dynamical theory of driven material systems and combining multi-scale models of defect and microstructure physics with complementary experimentation, on commensurate length scales. This unique combination of theory, computation and experiments will capture the complex interplay between the fission-induced defects and emerging microstructure with pre-existing grain structure, thus enabling the prediction of the impact of microstructure evolution on thermal transport in UO_2.

The Center brings together an internationally renowned, multi-institutional team of experimentalists and computational materials theorists focusing on understanding *microstructure science under irradiation*. The framework of non-linear dynamics of irradiation-driven materials will lead to an atomistically-informed generalized mesoscale phase-field model for the irradiation-induced microstructure evolution, which will furnish the defect state impacting thermal transport (see Fig. 1). This approach will capitalize on the team’s demonstrated strength in theoretical and computational modeling of materials at all scales. In close synergy with the modeling effort, the experimental team will perform advanced microstructure, thermal-transport, and mechanical-property measurements on UO_2 using the unique experimental capabilities of DOE user facilities, including the Advanced Test Reactor (ATR), the Spallation Neutron Source (SNS) and the High Flux Isotopes Reactor (HFIR), and the Advanced Photon Source (APS), in addition to an array of state-of-the-art characterization techniques.

The availability of the new ATR National User Facility at INL not only gives the Center a distinct local dimension but also provides the unique capability of tying all of the experimental investigations to a true fission environment. Indeed, the ultimate goal of the Center is to develop an in-pile measurement capability to monitor degradation of critical components of the fuel assembly. This will enable us to develop new predictive models that can be benchmarked against actual ATR fuel data.

Center for Materials Science of Nuclear Fuel	
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Florida State University	Anter El-Azab
University of Florida	Michele Manuel, Simon Phillpot
Colorado School of Mines	John Moore
University of Wisconsin	Todd Allen
Oak Ridge National Laboratory	Ben Larson, Gene Ice, Judy Pang

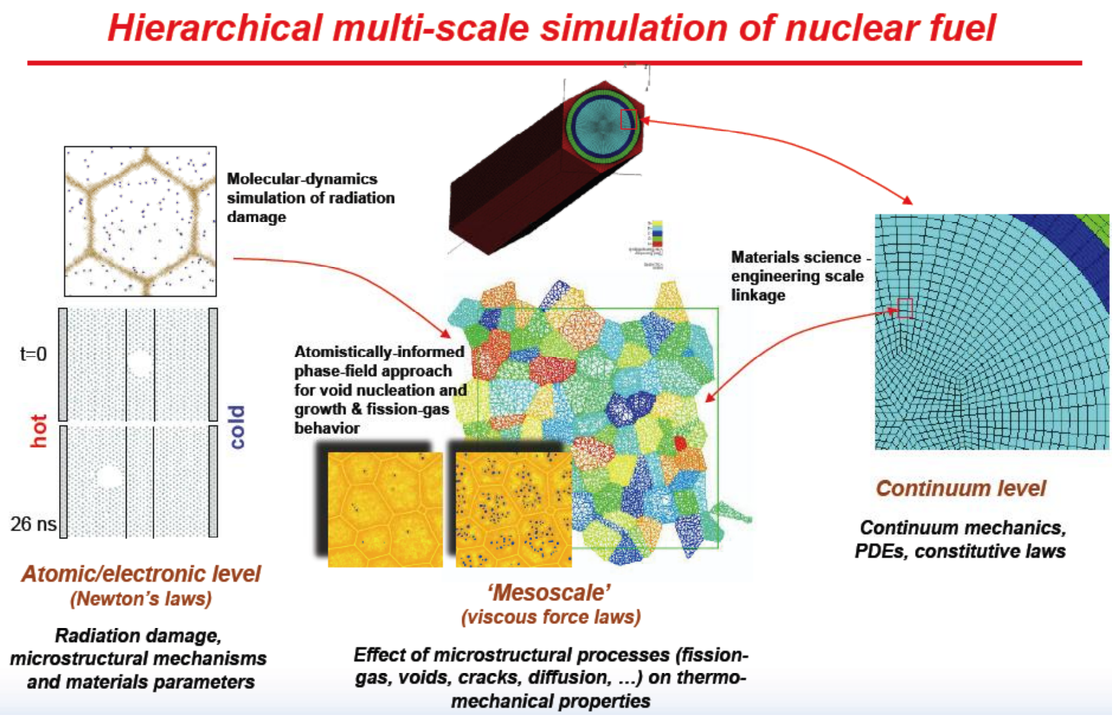

Fig. 1. The hierarchical multi-scale, multi-physics simulation approach developed through this EFRC combines three distinct levels:

- The ***atomic-level approach*** sketched on the left uses molecular-dynamics (MD) simulations in which the evolution of the system is followed based on the solution of Newton's equations of motion (typically over millions of time steps, or nanoseconds of real time).

- The quantified insights from the atomic-level simulations provide the input to the ***mesoscale approach*** based on a comprehensive phase-field model (center). The objects evolving in the mesoscale model are the microstructural elements such as the grain boundaries, dislocations, fission-gas bubbles, etc. The mesoscale elements evolve under the influence of thermodynamic forces. These ***atomistically-informed*** mesoscale simulations follow explicitly the evolution of the microstructure, typically over the order of milliseconds of real time.

- The output of the mesoscale simulations, "homogenized" in terms of net properties, such as the effective density, thermal conductivity and elastic moduli for a given state of temperature, stress and irradiation, serves as input into the ***continuum-level approach*** sketched on the right. The continuum calculations involve solution of a coupled set of partial differential equations, traditionally with materials input via empirical relations for the thermo-mechanical behavior of the material under the effects of irradiation. Here, via scale bridging down to the mesoscale, the continuum approach is ***microstructurally informed***.

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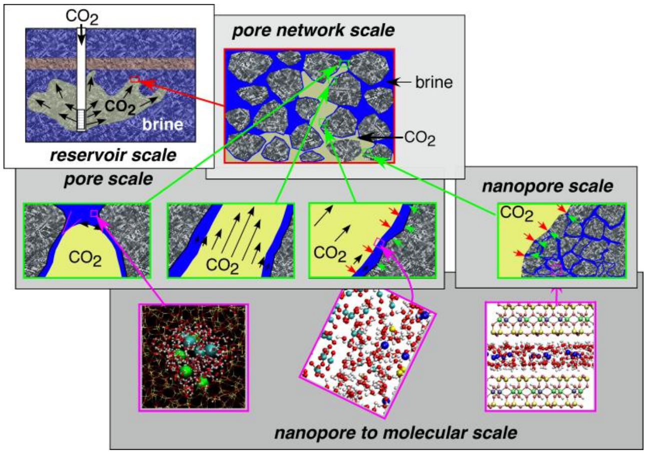
Center for Nanoscale Control of Geologic CO_2
EFRC Director: Donald J. DePaolo
Lead Institution: Lawrence Berkeley National Laboratory

Mission Statement: The mission of this center is to use new investigative tools, combined with experiments and computational methods, to build a next-generation understanding of molecular-to-pore-scale processes in fluid-rock systems, and to demonstrate the ability to control critical aspects of flow and transport in porous rock media, in particular as applied to geologic sequestration of CO_2.

Technical Overview: A combination of carefully integrated experiments and modeling approaches will be used to evaluate essential molecular and nanoscale processes, and to treat the transition from the nanoscale to pore scale, and the effects that arise at that scale. Multiscale computational models and lab-scale experiments will be used to understand the emergence of macroscale properties and processes. Unique BES experimental facilities at the primary work site, LBNL, together with facilities located at ORNL and LLNL, will be employed, as well as expertise in materials science, geochemistry, hydrology, biology and geophysics at these and associated academic institutions. The unique character of the center will derive from its integrated multidisciplinary approach, and a focus on directing CO_2-rich fluids.



The products of the Center will provide the fundamental knowledge necessary to develop a revolutionary level of control and predictive capability for subsurface fluids. It will help facilitate safe long-term storage of CO_2 in subsurface reservoirs to address the threats of global warming, and produce important advances related to fluid manipulation for other types of energy resource development and management**.**

The efforts of the Center investigators are grouped into three Thrust Areas: (1) controlling nucleation and growth, (2) nanopore processes, and (3) emergent processes. The three Thrust Areas, described in more detail below, represent groupings of investigators who use similar experimental approaches and whose work in the Center will be directed at closely allied scientific challenges. However, there are a large number of cross connections within and between these thrust areas. The three thrust or focus areas have three to six lead scientists, representing all of the institutions involved and constituting the management and scientific leadership of the Center. The lead scientists have extensive experience in designing, organizing, and executing both large and small research projects, and experience in managing laboratory science and coordinating research utilizing large DOE facilities. All key participants have had BES funding to pursue related studies and continue to be among the most productive and influential Earth scientists in the U.S.

Thrust Area 1 - Controlling nucleation and growth: The ability to seal deep reservoirs and prevent escape of gases and fluids is one requirement for geological CO_2 sequestration. Reservoirs may be sealed by the precipitation of new minerals in the pore space, or the seal may be maintained by suppressing mineral dissolution. It may also be desirable to control the rate at which mineral precipitation and dissolution occur relative to flow and transport so as to engineer the spatial distribution of reaction products. To manipulate the dissolution, nucleation and growth of minerals in the subsurface environment a detailed understanding of these processes and how they are affected by the special characteristics of porous rock media is required.

Research Topics:

- Inorganic controls on mineral nucleation, growth, and dissolution
- Alkaline earth oxide or hydroxide nanoparticles as embedded nutrients
- Biomimetic approaches to controlling carbonate mineralization
- Extremophiles for biotic control of carbonate mineralization

Thrust Area 2 – Nanopore Processes**:** Little is known about the chemical behavior of CO_2-rich aqueous solutions confined in nanopores under sequestration conditions. The overarching goal of research under Thrust Area 2 is to provide a fundamental understanding of these nano-confined fluid CO_2-aqueous solution mixtures using advanced methodologies that probe fluid behavior from molecular to pore scales.

Research Topics:

- Thermophysical properties of nano-confined CO_2-rich fluids
- Structure and dynamics of CO_2-bearing aqueous solutions in nanopores
- Structure and dynamics of CO_2/water interfaces and thin aqueous films

Thrust Area 3 – Emergent Processes: The injection of CO_2 into the subsurface environment drives the fluid-rock system into "far-from-equilibrium" conditions where new behavior may emerge that is not predictable by considering processes in isolation. This nonlinear response to the coupling of flow, transport, and reaction at multiple scales results in emergent structures and self-organization, an excellent example of which is the reactive infiltration instability. These emergent dynamics must be understood in order to predict how CO_2 will behave in the subsurface.

Research Topics:

- Emergent pore-scale dynamics resulting from coupling of multiphase flow, transport, and reaction Multiscale experiments combining X-ray microtomography and pore scale modeling
- Macroscale models from microscale physics and chemistry

Center for Nanoscale Control of Geologic CO_2 (NCGC)	
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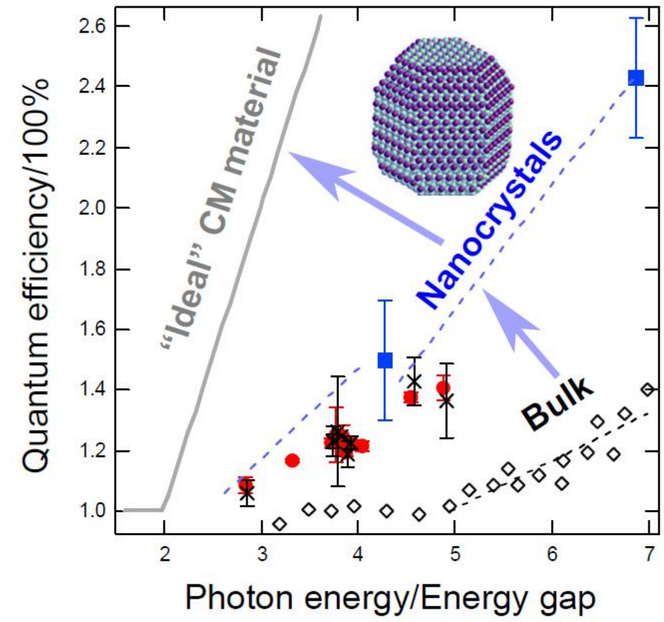
Center for Advanced Solar Photophysics
EFRC Director: Victor I. Klimov
Lead Institution: Los Alamos National Laboratory

The goal of this center is to explore and exploit the unique physics of nanostructured materials to boost the efficiency of solar energy conversion through novel light-matter interactions, controlled excited state dynamics, and engineered carrier-carrier coupling.

Practical means to approach or *exceed* the Shockley-Queisser equilibrium thermodynamic efficiency limit require advanced mechanisms of converting photons into electrical charges. Breakthroughs in solar energy conversion are expected to come not from iterative improvements of existing technologies but instead from discoveries of new physical phenomena and/or materials with engineered functionalities. The tailorable electronic properties and unique physics of ultrasmall matter in the form of both quantum-confined semiconductors and nanostructured metals are expected to offer new processes that could yield progress toward this goal.

The research of this Center concentrates in three main Thrust areas including: 1) Novel nanoscale physical phenomena for efficient capture and conversion of light into electrical charges via quantum confinement, plasmonic and photonic effects; 2) New means for charge manipulation in nano-assemblies for rapid charge extraction and low-loss transport; 3) Proof-of-principle solar-energy conversion schemes that exploit the emergent physics of the nanoscale size regime.



Carrier multiplication in PbSe nanocrystals. Photon-to-exciton conversion efficiencies in PbSe nanocrystals compared to bulk PbS. The grey line is the "ideal" efficiency as defined by energy conservation. One goal of this center is to understand the factors that control carrier multiplication efficiency. This would allow for the development of novel nanoscale materials with performance which approaches the ideal limit.

New physical principles for light harvesting and conversion into electrical charges that will be explored in the first Thrust involve carrier multiplication (generation of multiple excitons by a single absorbed photon), engineered densities of states in plasmonic and photonic structures, band-structure engineering in nanoscale semiconductors and dynamic control of energy gap via Coulomb interactions, among others. For instance, carrier multiplication can potentially improve the power conversion efficiency of low-cost single junction photovoltaics via production of enhanced photocurrent from blue to ultraviolet solar photons. Likewise, semiconductor-metal interactions in nanoplasmonic structures can be used to increase the absorbance of ultrathin semiconductor layers, extend the range of excitonic transfer, and tune the strength of carrier-carrier Coulomb coupling.

Effective exploitation of the unique properties of nanostructured materials in solar energy conversion, especially in utilizing multiple excitons or "hot carriers", is contingent upon our ability to efficiently extract and transport carriers to charge collecting electrodes. The "Charge-manipulation" Thrust will explore charge separation and transport as well as energy transfer in engineered nano-assemblies. Specific previously unexplored topics will include extraction of multiple charges, exciton transport in extended gradient structures, and the effects of semiconductor-metal interaction on energy transfer.

Finally, the development of prototype Generation-III devices that demonstrate enhanced power conversion efficiency through utilization of novel nanoscale physics and architectures is a key goal of this Center. The third Thrust vertically integrates our understanding of the unique physical principles at each step of solar energy capture and device function by developing and fabricating "exploratory" architectures. These architectures and prototype devices will be specifically designed to harness the physical principles found in both discrete and simple extended structures. Further, they will be used to elucidate key interfacial phenomena endemic to sequential increases in complexity, e.g., in progressing from a simple nanocrystal film to a multilayer device. We are focusing our studies on materials and structures amenable to scalable, low-cost fabrication and processing methodologies, such as solution-based synthesis, and on the development and refinement of compatible new techniques.

Key to each of these Thrusts is physics-driven synthesis. Promising nanoparticles and assemblies will be identified and developed based upon the most up-to-date understanding of the physics. Novel nanoparticle compositions, shapes, surface properties and hybrids will be targeted for their utility, whereas in assemblies, we will investigate novel means to functionalize and assemble materials for efficient function.

Center for Advanced Solar Photophysics(CASP)	
Los Alamos National Laboratory	**V.I. Klimov (Director)**, J.A. Hollingsworth, H. Htoon, Q. Jia, J.M. Pietryga, R.D. Schaller, M. Sykora, S. Tretiak
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University of California, Irvine	M. Law, J. Hemminger
Rice University	N.J. Halas, P. Nordlander
University of Minnesota	U. Kortshagen
University of Colorado	D. Jonas
Colorado School of Mines	P.C. Taylor

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Center for Materials at Irradiation and Mechanical Extremes
EFRC Director: Michael Nastasi
Lead Institution: Los Alamos National Laboratory

Mission Statement: To understand, at the atomic scale, the behavior of materials subject to extreme radiation doses and mechanical stress in order to synthesize new materials that can tolerate such conditions.

Our EFRC addresses two of the five BESAC grand challenges: *How do we design and perfect atom and energy-efficient syntheses of revolutionary new forms of matter with tailored properties?; and How do we characterize and control matter away-especially very far away-from equilibrium?* In responding to these grand challenges our center will focus on *Materials at Irradiation and Mechanical Extremes (MIME).* This Center recognizes that the challenge to developing materials with radically extended performance limits at irradiation and mechanical extremes will require designing and perfecting atom- and energy- efficient synthesis of revolutionary new materials that maintain their desired properties while being driven very far from equilibrium. We have developed a set of common issues that will drive our science focus and serve as the unifying foundation of this center. These scientific issues include: 1) Absorption and recombination of point and line defects at interface; 2) Morphological and chemical stability of interfaces; 3) Interface-driven mechanical response. By addressing these issues we will develop a fundamental understanding of how atomic structure and energetics of interfaces contribute to defect and damage evolution in materials, and use this information to design nanostructured materials with tailored response at irradiation and mechanical extremes.

In the pursuit of the grand challenge and science issues outlined above, we have developed specific hypotheses for each science issue. These defining hypotheses are listed below.

Scientific issue #1: *Absorption and recombination of point and line defects at interfaces*

Hypotheses:

1) The atomic structure of the interface controls the absorption, emission, storage and annihilation of defects at the interface.

2) Misfit dislocation intersections with other misfit dislocations and with disconnections are the most favorable sites for point defect absorption and delocalization.

3) The lower the elastic strain energy penalty associated with defect absorption, the more likely it is that point defect delocalization by interface reconstruction can take place.

4) The ability of an interface to absorb dislocations is determined by its shear strength and the areal density of preferred sites for nucleation of interface glide dislocations.

Scientific issue #2: *Morphological and chemical stability of interfaces*

Hypotheses:

5) Interface structures with high sink strengths or enhanced abilities to act as defect sources will be morphologically stable at extremes of temperature, irradiation and mechanical deformation.

6) Interface energy controls interface stability; high-energy interfaces are less likely to be morphologically stable.

7) The saturation limit for defect absorption at interfaces for a given type of defect (e.g., helium atom, solute segregant, vacancy, interstitial, dislocation) is determined by the interface structure. Above the defect solubility limit, interfaces exhibit chemical instabilities such as defect clustering, gas bubbles, precipitates, disordering or amorphization.

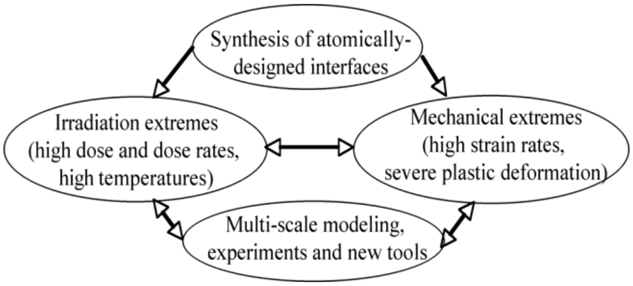
Scientific issue #3: *Interface-driven mechanical response*

Hypothesis:

8) The cohesive strength/mechanical damage evolution behavior for a given interface structure may change at high dose or high strain rates.

Using the above hypotheses, we have developed **quantitative figures-of-merit** for the defect sink strength of interfaces. These figures-of-merit will allow us to use a focused approach where model systems containing interfaces with high and low values of predicted sink strengths can be experimentally tested and the results used to refine the models.

The hypotheses driven research proposed in this center, will naturally have two focus areas (thrusts) dealing with the *role of interfaces* in: 1) *extreme irradiation environments*; and 2) *mechanical extremes*. Synergy will be enhanced through the development of new computational and characterization methods, and synthesis of common model systems. Materials will be synthesized via vapor deposition methods, solidification processing, diffusion bonding, and severe plastic deformation. Common theory, modeling, and simulation tools and methods will include *ab initio*, molecular dynamics (MD) and accelerated MD (AMD), kinetic Monte Carlo (KMC), rate theory calculations, and crystal plasticity modeling (large scale simulations will leverage LANL's supercomputer *Roadrunner*). New tools will be developed for extending our abilities to carry out multi-length and multi-time scale studies. This will include the development of a parallel off-lattice KMC, a hybrid MD/AMD/KMC method, and *in situ* ultra-fast laser and XRD characterization capabilities. The development of these methods will allow, for the first time, direct coupling of experimental measurements and computer simulations at comparable length and time scales. The integrated structure of the center is shown schematically in the figure below.



Materials at Irradiation and Mechanical Extremes (MIME)	
Los Alamos National Laboratory	**M. Nastasi (Director)**, A. Misra, G.T. Gray, S.A. Maloy, B.P. Uberuaga, C. P. Stanek, I.J. Beyerlein, N. A. Mara, T.C. Germann, E.K. Cerreta, A.F. Voter, S.M. Valone, S. Luo, K.J. McClellan, Q. Jia, D.A. Yarotski, D. Alexander, Y. Wang, R.M. Dickerson, P. O. Dickerson
Lawrence Livermore National Laboratory	A. Caro
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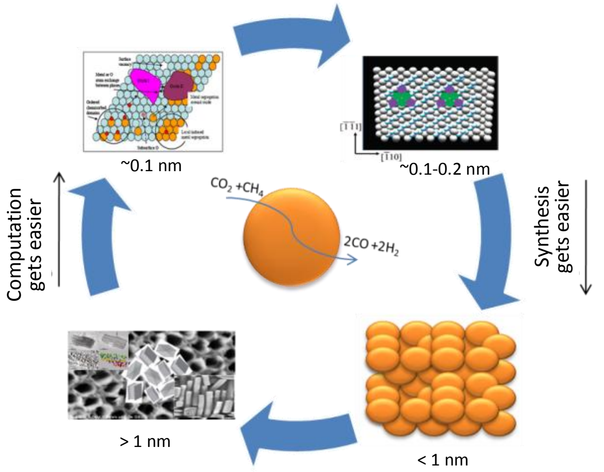
Center for Atomic-Level Catalyst Design

EFRC Director: James Spivey; Lead Institution: Louisiana State University



<u>Mission Statement</u>. Our mission is to extend the capabilities of current computational and synthesis/ characterization tools and complement those tools with new approaches to atomic level synthesis and characterization of catalysts that achieve highest activity and selectivity in energy conversion processes.

<u>Rationale</u>. Recent advances in computational catalysis, and in our ability to synthesize materials with structural control at extremely small length scales, hold tremendous promise for dramatic improvements in catalysis. Despite rapid progress in both areas, we do not yet have the ability to (a) computationally design an ideal catalyst for a reaction of reasonable complexity at conditions of practical interest, nor to (b) prepare the catalyst with a degree of atomic-level precision that mimics the surfaces that we can simulate by computation.

This gap between simulated (computational) and real world catalysis can be visualized in a number of ways, e.g., by comparing the degree of difficulty in (a) calculating the interactions of even simple molecules with extremely small metal clusters and (b) in synthesizing these same clusters in a completely controllable way. Assuming other factors are constant (such as the complexity of the reaction), as the size of the active catalyst increases and the level of control over the atomic-level structure of the surface decreases, catalyst synthesis becomes easier—but the computational description of the catalyst (especially under reaction conditions) becomes less realistic—often because simplifying assumptions must be made that cannot be verified. Although the absolute length scale representing the limits of computation or synthesis may vary for different metals and reactions, the point is clear—there is a <u>gap</u> in our ability to identify an ideal catalyst by computation and to then prepare and characterize it unambiguously (Figure-1).

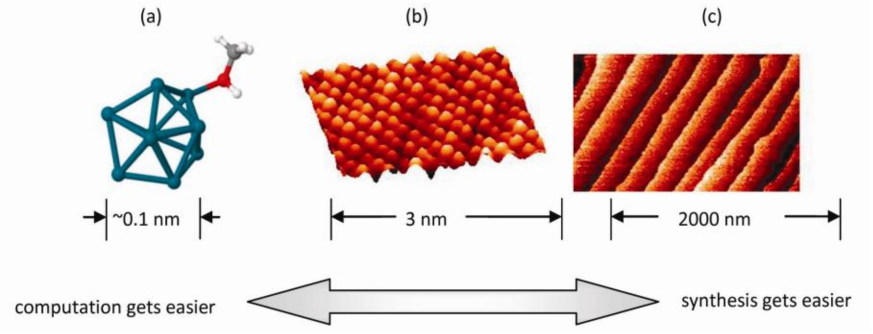


Fig. 1. Difficulty of computational and synthesis/characterization research vary in opposite directions with length scale; (a) CH_3OH on Rh_7 cluster (DFT model by D. Bruce, Clemson Univ.); (b) $Pt_{25}Rh_{75}(100)$ Alloy 3-d topography (www.omicron.de); (c) Mono-atomic steps on SiO_2SiO_2 layer - in UHV at T = 800 K in AFM mode.

Approach. Our approach is two-fold; (a) extend the capabilities of current computational and synthesis/characterization tools and (b) complement those tools with newly developed approaches to synthesis and characterization. The computational effort will focus on developing first-principle based multi-scale models to predict catalytic behavior by following the dynamic evolution in both composition and structure over experimentally relevant time and length scales. The morphological changes and reactivity of the catalyst under various realistic conditions will be explored and the modeling predictions will be validated by experimental data. While Density Functional Theory (DFT) has been a very useful complement to surface science experiments, our proposed multi-scale modeling will be a step towards a more predictive role for computational simulations.

The synthesis effort is intended to extend--to ever-smaller dimensions--the length scales at which precise, computationally-specified structures of supported metals can be prepared. The approach will be an iterative process using synthesis and computation, in an integrated fashion. The proposed approach is anticipated to challenge the limits of both synthetic tools and computational techniques employed.

Center for Atomic-Level Catalyst Design	
Louisiana State University	**James Spivey (Director)**, C. Kumar, W. Plummer, R. Kurtz, P. Sprunger, K. Dooley G. Griffin, J. Flake
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Texas A&M University	D.W. Goodman
Georgia Tech	D. Sholl
University of Utrecht, Netherlands	K. P. de Jong, J.H. Bitter, P.E. de Jongh
University of Florida	S. Sinnott, A. Asthagiri
UT-Batelle/ORNL	Y. Xu
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Tulane University	U.Diebold
Penn State	M. Janik

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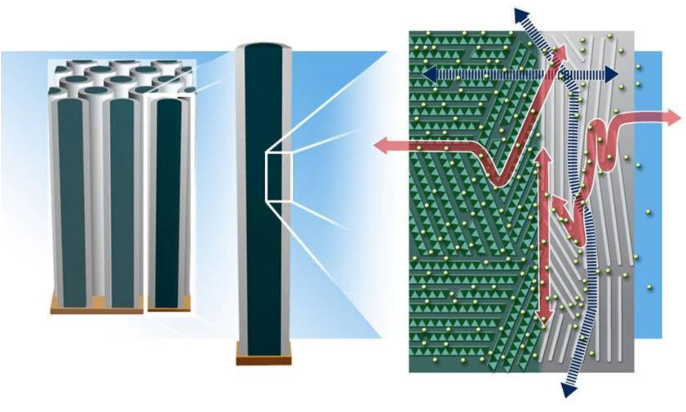
Center for Science of Precision Multifunctional Nanostructures for Electrical Energy Storage (NEES)
EFRC Director: Gary Rubloff
Lead Institution: University of Maryland

Mission: The goal of the EFRC is to provide the scientific underpinnings for a new generation of electrical energy storage devices that will deliver dramatic improvements in power (10-100X) and energy density (10X).

The EFRC envisions multifunctional nanostructures as the answer to this challenge, suitably designed for facile, repeatable and bidirectional transport of ions and electrons between high capacity nanostructures (e.g., nanowires) and remote contacts to the external world. At the same time, the storage materials must be capable of accommodating large ion densities which cycle in and out of the storage material in a robust, virtually self-healing fashion that preserves the nanostructure of the host. To meet the multifunctional requirements of fast charge transport, high charge storage density, and stability in these functions during extensive cycling of charge, we believe that well-defined and well-controlled heterogeneous nanostructures are essential, composed of multiple materials and realized in specific geometries. These requirements furthermore pose fundamental scientific challenges in kinetics, structural dynamics, and thermodynamics on the nanoscale.

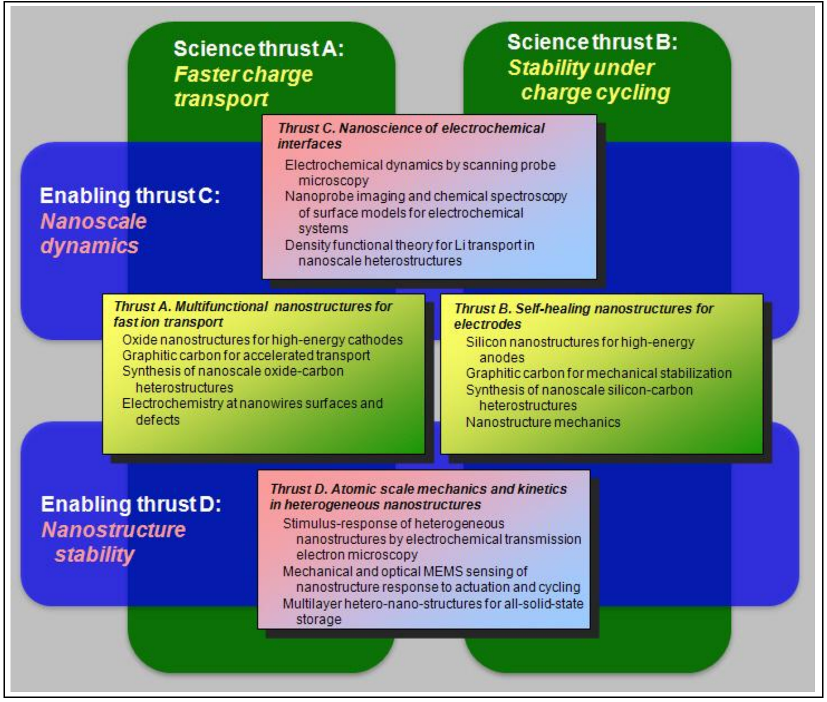
We have identified low-dimensional carbon as a vehicle to assist rapid charge transport and to stabilize structures under cycling of high charge concentrations. Heterogeneous nanostructures of carbon and charge storage materials (oxide-based cathodic and Si-based anodic structures) will be investigated to understand their fundamental behavior in charge transport and storage.



Schematic of nanostructured heterogeneous electrode with separate ion storage and electron transport layers.

To enable these research advances, the EFRC will pursue new approaches to elucidating fundamental nanostructure electrochemistry, including the chemistry and electrochemistry of model systems (defect sites, specific molecular interactions) and accompanying theory. It will also develop new measurement strategies, including microsystems for using in-situ high resolution transmission electron microscopy (TEM) during electrochemical reactions and novel cantilever structures to infer nanostructural changes. Microsystems for in-situ electrochemical TEM will be developed and exploited as a Discovery Platform in SNL-LANL's Center for Integrated Nanotechnologies (CINT), thus available to a wide audience.

The EFRC also places a priority on precision, regular nanostructures whose geometry and composition are predictable and optimized. This is well suited to application of new characterization approaches and ultimately to viability of the nanostructures for application in massive parallel arrays as needed for a next-generation, nano-enabled electrical energy storage technology.



The EFRC is organized as four thrust areas. Two science thrusts will drive the EFRC's scientific inquiry, addressing the fundamental issues of charge transport kinetics in multifunctional, multicomponent nanostructures and structural stability under charge cycling. Complementary enabling thrusts will support science to uncover nanoscale dynamics both experimentally and theoretically, and provide new instrumentation strategies to observe nanostructure stability metrics during charge cycling. Synthesis techniques for heterogeneous nanostructures, shared commitment to carbon as part of the nanostructures, and multiple perspectives on how to elucidate nanoscale electrochemistry in these structures present common ground for the two science thrusts, while the two enabling thrusts find shared interest in revealing and understanding electrochemistry and structure at the nanoscale. The science and enabling thrusts are tightly linked as well, with the former providing test structures to be characterized and understood by the latter, and in turn the enabling thrusts delivering feedback on nanostructure design to the science thrusts.

Center for Science of Precision Multifunctional Nanostructures for Electrical Energy Storage (NEES)	
University of Maryland, College Park	**G.W. Rubloff (Director)**, S.B. Lee, M. Fuhrer, J. Cumings, R. Ghodssi, J. Reutt-Robey, C. Wang, Y. Wang, E. Williams
Sandia National Laboratory, Albuquerque	R. Hwang, J. Sullivan, J. Huang, K. Zavadil, K. Leung
University of California Irvine	R. Penner, P. Collins
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Center for Excitonics
EFRC Director: Marc Baldo
Lead Institution: Massachusetts Institute of Technology

Mission Statement: A comprehensive center for the science and technology of excitons.

Excitons are the crucial intermediate for energy transduction in low cost, disordered semiconductors. In this center, we seek to supersede traditional electronics with devices that use excitons to mediate the flow of energy. The problem with conventional electronic devices is that they are difficult to manufacture; their constituent materials require very high levels of order and achieving such low entropy in a semiconductor requires expensive and energy intensive fabrication. For example, the energy payback time for a crystalline silicon solar cell is on the order of 2 years, and at current manufacturing growth rates, it is expected to take at least 20 years to produce enough silicon-based solar cells to make a significant impact on the world energy supply. Similarly, epitaxial growth constraints are likely to limit solid state lighting sources to a small fraction of the overall demand for lighting.

There is an alternate approach that is more suitable for large scale production. We will use materials with only short-range order. Such *nanostructured* are compositions of nano-engineered elements such as organic molecules, polymers, or quantum dots and wires, in films bound together by weak van der Waals bonds. These materials are characterized by *excitons* that are *localized* within the ordered nanostructures. Due to localization of the excited states, the optical properties of the films are relatively immune to longer-range structural defects and disorder in the bulk. And in contrast with the painstaking growth requirements of conventional semi-conductors, weak van der Waals bonds allow nanostructured semiconductors to be readily deposited on a variety of materials at room temperature.

Figure 1. An excitonic circuit in photosynthesis. Like our nanostructured devices, photosynthesis exploits excitons and exhibits much larger levels of long range disorder than conventional solar cells. Image: Sundstrom, *et al*. J. Phys. Chem. B **103**, 2327 (1999).

We seek to solve two grand challenges in excitonics.

Exciton Transport:

Controlling the transport of excitons is the first major thrust of the center. In this center we will develop new theory to explain and model the movement of excitons in complex nanostructures. We will build artificial excitonic antennas that absorb and guide light in nanofabricated circuits of molecular chromophores, J-aggregates, quantum dots and nanowires. We will characterize coherence and energy transfer in our antennas using scanning probe microscopy and our recently developed technique of fully phase coherent

2-d Fourier transform spectroscopy. Finally, our excitonic technologies will be applied to low cost solar cells and luminescent solar concentrators, which promise power efficiencies > 30%.

Exciton Dynamics:

The second major thrust is to control the creation and destruction of excitons. In this center we will develop new theory for the dynamics of exciton formation and separation. Applications include increasing the efficiency of organic light emitting devices by up to a factor of four and characterizing the fundamental efficiency limits of excitonic solar cells. We will develop two important tools that are unique to the center: Cathodo-luminescence Scanning Transmission Electron Microscopy (CL-STEM), which will be used to characterize the structure-function relationships of excitonic nanomaterials, and Superconducting Nanowire Single-Photon Detectors (SNSPDs). SNSPDs can conclusively determine the efficiency of multiple carrier generation, a process with enormous potential for solar cells. Finally, we will characterize the link between exciton annihilation and device degradation.

Center for Excitonics	
Massachusetts Institute of Technology	**M.A. Baldo (Director)**, P.I. Barton, M.G. Bawendi, K.K. Berggren, V. Bulovic, S. Gradecak, J. Kong, K.A. Nelson, R.J. Silbey, T.M. Swager, T. Van Voorhis
Harvard University	A. Aspuru-Guzik, K. Crozier
Brookhaven National Laboratory	C. Black, P. Sutter

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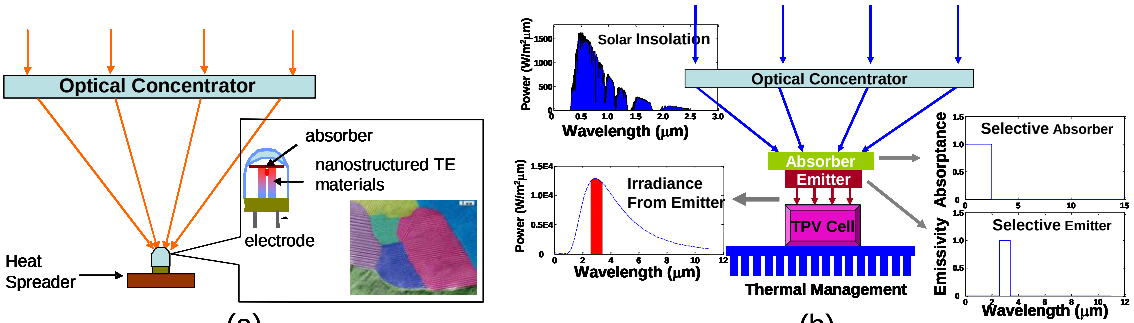
Solid-State Solar-Thermal Energy Conversion Center (S^3TEC Center)
EFRC Director: Gang Chen
Lead Institution: Massachusetts Institute of Technology

Mission Statement: S^3TEC Center is to become an intellectual base to develop transformational solid-state solar-thermal to electric energy conversion technologies by advancing fundamental science of energy carrier coupling and transport, and to use the fundamental understanding to design new materials and devices to achieve a leapfrog in efficiency, to develop cost-effective manufacturing processes for energy conversion materials, devices, and systems, and along the way, to develop new interdisciplinary approaches for nano and energy workforce training, foster nano-energy based enterprises, and enhance the public awareness of the societal impacts of nanotechnology and engage them in energy conservation.

The S^3TEC Center aims at advancing fundamental science and developing materials to harness heat from the sun and convert this heat into electricity via solid-state thermoelectric (Fig. 1a) and thermophotovoltaic (Fig.1b) technologies. Solar thermophotovoltaics (STPV) first use solar radiation to raise the temperature of a terresterial object, which then emits photons optimized to the bandgap of a photovoltaic cell to generate electricity. Solar thermoelectric energy conversion uses solar radiation to create a temperature difference across a solid-state material to generate electricity. These technologies have transformative potentials: solar thermophotovoltaics have a theoretical maximum efficiency of 85% with a single junction photovoltaic cell, while solar thermoelectrics could potentially reduce solar electricity generation cost below \$0.5 per electrical watt (W_e), compared to silicon based PV cells currently at \$3-4/W_e. Thermoelectrics can also be used in combination with current solar technologies. Both thermoelectric and thermophotovoltaic technologies can be applied to terresterial heat sources, for example, geothermal, waste heat from industrial processses, transportation and buildings. Thermoelectric devices can also be used for refrigeration and air-conditioning without producing any greenhouse gases.

The efficiency of solar thermoelectric generators (STEG) depends on spectrally selective surfaces with a high absorptance to the solar radiation and a low emittance in the infrared range, and depends on the availability of thermoelectric materials with high figure of merit, which is linearly proportional to the electrical conductivity, the square of the Seebeck coefficient, and inversely proportional to the thermal conductivity. The S^3TEC



(a) (b)

Figure 1 Solid-state solar-thermal energy conversion technologies to be pursued at the S^3TEC Center (a) low-cost solar thermoelectric generators (STEGs) built from high performance nanostructured thermoelectric materials, and (b) high efficiency solar thermophovoltaics achieved via precision spectral control.

center aims at advancing thermoelectric materials through detailed experimental and theoretical studies of electron and phonon transport in nanostructures and bulk materials. Optical pump-probe and neutron scattering will be used to understand phonon transport, together with quantum and classical simulation of phonon transport in bulk and nanostructured materials. Electron spectroscopy will be performed in both thermoelectric materials and at the electrical contact regions, together with transport modeling. Both thin films and bulk nanostructures will be investigated, aiming at eventual large scale applications. Prototypes will be built to demonstrate the potential of the solar thermoelectric generation. Neutron spectrometers and STEM at Oak Ridge National Laboratory will be used for phonon spectroscopy and high-resolution imaging of interfacial structures. Ultraviolet photoelectron spectroscopy at Brookhaven National Laboratory (BNL) will be employed to measure the work function of the developed thermoelectric materials and contacting electrode materials.

Spectral control is not only important for STEG, but also crucial for STPV. Ideal selective absorbers should absorb all solar radiation, but not lose heat via their own thermal emission. In a solar TPV, broadband solar insolation is first absorbed by a surface, which heats the absorber to 1000-2000 ^{o}C. On the other side of the absorber is an emitter, which reradiates photons that are optimized to match a photovoltaic cell. The maximum efficiency of such solar TPV converters is 85.4%, very close to that of multijunction cells with an infinite number of stages (86.8%), but it can be achieved with a single junction cell. Selective surfaces for solar TPV are more challenging due to their higher operational temperature. Key questions for solar TPV are: (1) How we can push structure design to reach the theoretical limit for selective absorbers and emitters? (2) Will the structure be stable at operational temperature? (3) How we can achieve high performance selective surfaces at low cost. And (4) how can we deliver high photon flux in a narrow spectral band. Our proposed research includes selective absorber and emitter design, fabrication, testing, high temperature stability studies for both thermoelectric materials and spectral control structures, and solar TPV prototyping.

The S^{3}TEC education/outreach initiatives will focus on training the next generation of energy science, technology, and entrepreneurship leaders; integrating research with education; attracting women and minority students into engineering and towards advanced engineering degrees, helping industry improve their energy efficiency, and creating new jobs.

Solid-State Solar-Thermal Energy Conversion Center (S^{3}TEC Center)	
Massachusetts Institute of Technology	**G. Chen (Director)**, M.S. Dresselhaus, E.A. Fitzgerald, J. Joannopoulos, J.G. Kassakian, S.-G. Kim, K. A. Nelson, Y. Shao-Horn, C.A. Schuh, M. Soljacic, and E.N. Wang
Boston College	C.P. Opeil and Z.F. Ren
Oak Ridge National Laboratory	O. Delaire and D.J. Singh

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Polymer-Based Materials for Harvesting Solar Energy

Thomas P. Russell and Paul M. Lahti, Co-Directors

University of Massachusetts Amherst

Mission Statement

The goal of the EFRC at the University of Massachusetts Amherst is to maximize the efficiency in the collection and harvesting of energy over a broad frequency range of the solar spectrum, while minimizing exciton recombination, maximizing electron transport across inorganic/organic interfaces, and optimizing the design and fabrication of inexpensive devices.

Center Research Portfolio:

The University of Massachusetts EFRC integrates the research of 17 investigators through three distinct Energy Research Groups or ERGs: ERG 1 *Polymer Based Architecture: Design and Synthesis*, ERG 2 *Controlled Assemblies and Morphologies*, ERG 3 *Photophysical Characterization, Device Design and Integration*. The synthetic efforts in ERG 1 will be complemented by collaboration with the Global Research Laboratory at Seoul National University and the University of Bayreuth. Theoretical studies will be pursued in ERG 2 of hierarchal ordering in promising composite materials with the University of Pittsburgh, and on exciton dissociation at organic-organic and organic-inorganic interfaces with the Oak Ridge National Laboratories. Efforts in ERG 3 will be augmented by collaborators at the University of Massachusetts Lowell and Konarka. The preparation of anatase titania nanorods and nanotubes will be done at the Pennsylvania State University and of inorganic nanoparticle and nanorod synthesis and assembly in the World Premier Institute, Advanced Institute of Materials Research at Tohoku University. The efficiencies of the devices produced by this EFRC will be evaluated and benchmarked at the National Renewable Energy Laboratory.

ERG 1 researchers will synthesize structures applicable to light harvesting and photocurrent generation, with a global objective of preparing fundamentally new electronically active materials with optimizable photophysical properties, and integrating them into the active layer of photovoltaic devices. A unifying objective of the synthetic strategy is to provide a range of polymer and nanocomposite materials geared towards morphological and photovoltaic device studies undertaken in ERGs 2 and 3. Synthetic efforts will utilize features of self-assembly, morphology, processibility, and charge transport, providing EFRC researchers with materials that contain tunable photophysical features, and that lead to more efficient photovoltaic devices.

ERG3 The primary research thrusts of this group fall into two main areas. The first is the synthesis of conjugated homopolymers, block copolymers, segmented structures and materials with well-defined structural architectures, with control over component energy levels using electron withdrawing and donating functionality. The second is the preparation of p-type conjugated polymers with end-groups suitable for functionalization of n-type nanoparticles and nanorods, leading to effective dispersion of the particles and rods, and the preparation of hierarchically oriented nanomaterial assemblies for devices.

ERG 2 The design and fabrication of a high-efficiency photovoltaic device requires precise control over the nanoscale morphology, molecular ordering, and interfacial properties of all components comprising the device. While obvious in statement, in practice, these tasks are quite challenging; most research on polymer-based photovoltaic devices to date has systematically considered at most one of these details. Researchers in ERG 2 integrate expertise in the synthesis, theory and engineering of polymers with established track records in controlling the self-assembly of polymers and the manipulation of polymer morphologies and individual chains in thin films. This expertise will be used to develop routes to control the morphology and structure of polymer-based and polymer/inorganic-based hybrid photovoltaic devices so as to optimize efficiency. The knowledge gained from these studies will then be used for device fabrication.

ERG 3 In an organic solar cell, the conversion of light energy to electric current involves five fundamental processes, (1) the absorption of light to create excitons, (2) the diffusion of excitons to a region of high electric potential mismatch where charge separation can occur, (3) charge separation, (4) charge transport of the holes and electrons to their respective electrodes, and (5) transport of the carriers across the respective organic-electrode interfaces (see **Figure 1**). All of these processes have to be understood individually to be able to optimize them for high efficiency solar cells. Detrimental effects, including charge carrier recombination and trapping, also need to be assessed to build structures that inhibit these effects. Associated with many of those processes are characteristic times scales that can be extremely fast (down to femtoseconds), particularly in nanoscale systems like the ones proposed in ERG 1 and ERG 2, since the distances involved are so small. Using time-resolved optical techniques it is possible to distinguish and quantify exciton lifetimes, charge separation dynamics, and electron and hole lifetimes that affect processes.

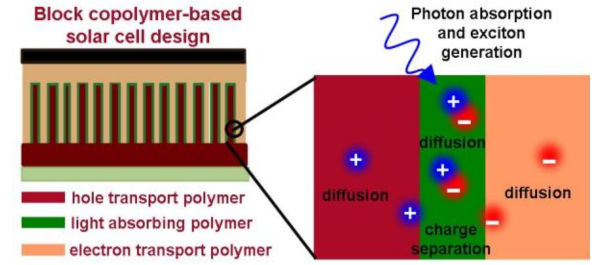

Fig 1 : *Illustration of the various processes that we will study with ultrafast optical spectroscopyic techniques.*

The primary goal of ERG 3 will be to elucidate photophysical details of charge and energy transport within nanostructured PV composite films. Single-molecule spectroscopy and ultrafast spectroscopy will provide valuable mechanistic insight and feedback to the synthetic components of our center as to the role of molecular architecture and confinement geometry on primary processes in PV systems. Using this information, ERG 3 will also provide working PV cell characterization using device absorption and efficiency measurements. Device fabrication and additional testing will be done by ERG 3 in collaboration with UMass Lowell and Konarka.

Polymer-Based Materials for Harvesting Solar Energy (PHaSE) (Lead Personnel)	
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University of Pittsburgh	**A.C.Balazs**
The Pennsylvania State University	**C. Grimes**
University of Massachusetts Lowell	**J. Kumar**
Oak Ridge National Laboratory	**R. Sumpter**
National Renewable Energy Laboratory	**D. Ginley**

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CENTER FOR SOLAR AND THERMAL ENERGY CONVERSION (CSTEC)

Peter F. Green
University of Michigan, Ann Arbor, MI

The goal of the center is to develop the science necessary to elucidate and mitigate energy loss processes in low dimensional, and/or complex nanostructured, organic, inorganic, and hybrid materials for *high efficiency* photovoltaic (PV) and thermoelectric (TE) energy conversion.

PV and TE energy conversion processes are controlled, in part, by the dynamics and interactions between charge carriers and phonons. In PVs, the transfer of energy from photons to electrons occurs through a series of identifiable stages: charge separation, diffusion, charge transfer, charge separation and finally harvesting (Fig. 1). Each stage is characterized by different length scales (0.1 nm-10^2 nm) and time scales (10^{-9}-10^{-15} s) and involves intrinsic energy losses. The interconversion between heat and electricity in TEs is characterized by the figure of merit, ZT. $ZT=S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electronic conductivity and κ is the thermal conductivity, which is controlled by the dynamics of phonons and charge carriers. Enhancing ZT requires decoupling $S^2\sigma$ and κ through nano-structural design. The research will involve cross-cutting efforts in theory, computation, materials growth/synthesis/fabrication, and physical property measurements, including the use ultrafast optical spectroscopy techniques. This effort will lead to a fundamental understanding of the dynamics and interactions of charge carriers and phonons, which is essential to control and to "tailor" the conversion efficiencies of low dimensional, and/or complex nanostructured, organic, inorganic, and hybrid materials for TE and PV applications.

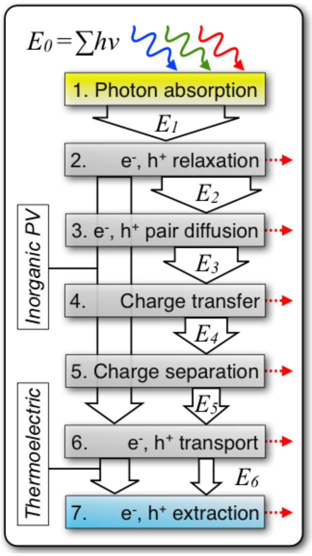

Figure 1: An illustration of the multi-step light-to-electricity conversion processes for organic PV, inorganic PV, and thermoelectrics. The loss mechanisms at each step are also described.

Research on *inorganic PVs* will focus primarily on low dimensional materials, including arrays of quantum dots and rods. Low dimensional and nanostructured materials show exceptional promise for high efficiency energy conversion. These materials will be fabricated using various self-assembly and patterning strategies, including focused ion beam nanopatterning and selective-array epitaxy. By varying the sizes and the spatial locations of dots and rods in 2D and 3D, the interactions between them may be controlled. The densities of electronic states increase with reduced dimensionality. Moreover, the carrier/phonon interactions, photon absorption/emission, electron/hole recombination and transport are necessarily controllable under conditions of reduced dimensionality and spatial organization. Intermediate band semiconductors, specifically dilute semiconductor alloys, will be considered in this study. Intermediate band- semiconductors are advantageous for overcoming intrinsic losses, associated with thermalization and absorption, experienced by *p-n* junction solar cells. Through a combination of density functional theory (DFT) and molecular simulations, a fundamental understanding of the energy conversion processes will be developed, leading to a series of materials design rules.

Organic PV materials present unique challenges and opportunities for improved efficiency and lower cost. Research will focus on thin-film systems comprising: (1) novel small molecules; (2) conjugated linear chain polymers; (3) dendritic and (4), caged molecules in which the chemical functionalities can be controlled. Self-assembly and patterning strategies will be used to control film morphology (e.g. length scales of phase separation, molecular ordering), which in turn can enhance exciton and charge carrier transport and separation. Molecular dynamics simulations and DFT will accompany chemical synthesis and thin-film processing, and help interpret measurements of ultra-fast energy conversion processes at organic-organic and organic-inorganic interfaces.

The overall aim of our thermoelectrics effort will be to study the fundamental mechanisms that can increase the ZT of a material by maximizing the Seebeck coefficient and electronic conductivity, while minimizing thermal conductivity. Nanostructuring and changes in dimensionality will be used to control carrier and phonon transport, as well as carrier/phonon interactions. Reducing the dimensionality leads to singular features, and enhanced response in the densities of electronic states. Nanostructuring, as well as reduced dimensionality, leads to enhanced scattering of mid-range frequency phonons, which are responsible for heat transport. Conjugated single molecules, specifically metal-molecule-metal junctions, will be investigated for TE applications. Because charge transport is controlled by discrete energy levels, the Seebeck coefficient in conjugated molecules is expected to be large; the thermal conductance is expected to be low due to the significant mismatch between the vibrational spectrum of the molecule and the metal. Simulation and modeling will provide critical insights into the relationship between nano-structure and transport mechanisms, and thereby provide guidance for the structural design of the next-generation TE materials.

The issues associated with nanostructuring TE and PV devices to achieve high energy conversion efficiency are very similar. By manipulating dimensionality of materials structures, their chemical composition, and building block functionality, the dynamics and interactions of phonons and charge carriers can be controlled and studied in both spatial and temporal regimes. In particular, we will utilize advanced ultrafast optical spectroscopy techniques to investigate these processes over a wide range of time scales in different classes of materials. In addition, the molecular and electronic structure of these materials will be determined using a combination of state-of-the art microscopies, x-ray diffraction, and neutron scattering techniques, complemented by detailed computer simulations.

In summary, through combined experimental, theoretical, and computational efforts, we will discover and develop the science associated with energy conversion mechanisms in photovoltaic and thermoelectric devices, fabricated using materials (inorganic, organic, and hybrid organic/inorganic) that possess low-dimensional and/or complex nanostructures. As outcome of our research we will have critically addressed the grand scientific challenges associated with: (1) control of materials processes at the level of electrons; (2) understanding and controlling properties of matter that emerge from the complex correlations of atomic or electronic constituents and (3) characterizing and controlling matter away from equilibrium.

CENTER FOR SOLAR AND THERMAL ENERGY CONVERSION (CSTEC)	
Institution	University of Michigan, Ann Arbor
Director	Peter Green
Principal Investigators	Roy Clarke, Barry Dunietz, Steve Forrest, Rachel Goldman, Theodore Goodson III, John Kieffer, Jinsang Kim, P.C. Ku, Ted Norris, Xiaoqing Pan, Kevin Pipe, Max Shtein, Ctirad Uher
Senior Investigators	Eitan Geva, Sharon Glotzer, L. Jay Guo, Massoud Kaviany, Nicholas Kotov, Richard Laine, Anne McNeil, Joanna Millunchick, Jennifer Ogilvie, Jamie Phillips, Pramod Reddy, Katsuyo Thornton, Anton Van Der Ven, Steve Yalisove

Contact: Peter F. Green, University of Michigan, pfgreen@umich.edu

Revolutionary Materials for Solid State Energy Conversion

EFRC Director: Donald T. Morelli

Lead Institution: Michigan State University

Mission Statement: The mission of this Center is to investigate, at a most fundamental level, the physical and chemical principles that will allow the understanding of how advanced thermoelectric materials function and the design and synthesis of such materials.

The **Center for Revolutionary Materials for Solid State Energy Conversion** will focus on solid state conversion of thermal energy to useful electrical power, both to increase the efficiency of traditional industrial energy processes and to tap new unused sources of energy such as solar thermal. Additionally materials with enhanced thermoelectric properties will find application in high efficiency, environmentally benign climate control systems. Our team represents some of the most experienced and capable researchers spanning all aspects of thermoelectric science from the design, synthesis and characterization of materials through the development of thermoelectric devices and systems. We will undertake a broad-based effort in semiconductor energy conversion materials utilizing and combining experimental, theoretical, and computational efforts. While ultimately the solution to the energy challenge is a technological one, beginning to solve this problem will take a serious effort at understanding physical processes at an elemental level. Our focus, therefore, will be on the fundamental aspects of thermoelectricity, which have their origin in physical processes occurring on the atomic scale. A major focus of our effort will be in the synthesis of new forms of matter, including both single phase alloys and compounds and composite structures created using nanoscience.

In order to meet the overall objective and mission of our Center, we have chosen to attack this problem from several different perspectives in terms of materials and fundamental processes. However these approaches share two common guiding principles and unifying objectives:

i. meet the challenge of lowering the thermal conductivity of thermoelectric materials to a minimum possible value;

ii. target the much more difficult task of increasing the thermoelectric power factor by manipulation of the electronic density of states of materials systems.

Ultimately, by working together in this Center we aim to develop design rules to predict properties of advanced thermoelectric materials, and realize these structures through innovative synthesis and advanced structural as well as chemical characterization.

We have organized our EFRC to have six main thrusts. The first four thrusts are directed at four broad categories of materials. In addition to these materials thrusts, our Center will recognize the importance of the characterization of the physical properties of new thermoelectric materials. Further, while the research is fundamental in nature, our aim is ultimately to develop new thermoelectric materials for use in devices with high conversion efficiency for power generation spanning the temperature range 0 - 700°C. Such thermoelectric materials and the devices and systems built up from them are expected to have myriad applications, including, for instance, auxiliary generators, waste heat recovery systems for vehicles, and solar thermal energy conversion systems. For these reasons, we also include effort aimed at understanding fundamental scientific issues related to thermoelectric devices and systems.

The six main thrusts of the Center are:

I. cubic nanostructured chalcogenides
II. self-assembled nanostructures
III. transition metal alloys with gaps and wells in the electron density of states
IV. semiconductors with resonant energy levels
V. thermoelectric and mechanical characterization of new thermoelectric materials
VI. fundamental scientific issues related to thermoelectric devices and systems

Work in these thrusts will be highly interdisciplinary and will involve all aspects of the experimental, theoretical, and computational capabilities available to us. For example, synthesis of bulk nanostructured chalcogenides (**Figure 1**) can be modeled computationally, structurally studied using advanced TEM and laser-assisted tomography, and characterized for thermoelectric and thermomechanical properties. An important part of our effort will involve the use of facilities at the Oak Ridge National Laboratory High Temperature Materials Lab (ORNL-HTML).

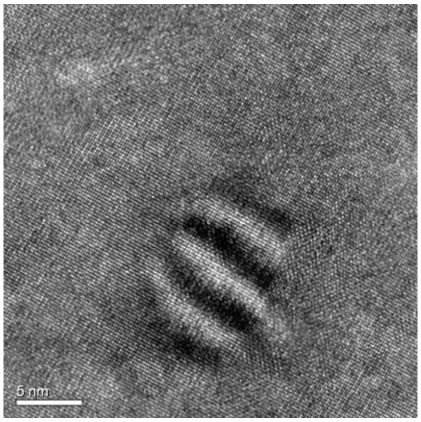

Figure 1 High resolution TEM image showing spinodally decomposed regions in PbTe-16%PbS.

Revolutionary Materials for Solid State Energy Conversion (RMSSEC)	
Michigan State University	**D.T. Morelli (Director),** E.D. Case, T. Hogan, S.B. Mahanti, J. Sakamoto, H.J. Schock
Northwestern University	V. Dravid, M. Kanatzidis, D. Seidman, C. Wolverton
Oak Ridge National Laboratory	R.B. Dinwiddie, E. Lara-Curzio, H. Wang
Ohio State University	J.P. Heremans
University of Michigan	C. Uher
University of California-Los Angeles	V. Ozolins
Wayne State University	S. Brock

Contact: Donald T. Morelli
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Center for Inverse Design
EFRC Director: Alex Zunger
Lead Institution: National Renewable Energy Laboratory

Mission: *Achieve the grand challenge of materials and nanostructures by design*: *Given the desired, target property, find the structure/configuration that has it, and then make the material.*

Historically, the development of new materials for technological applications has been based to a large extent on trial-and-error searches or accidental discoveries. This pattern is exemplified not only by the historic discovery of semiconductivity in Si and GaAs, but also, more recently, by the discovery of new materials with unsuspected physical and chemical properties, including: high-T_C in cuprates or iron-based superconductors, high tensile strength in carbon nanotubes, and colossal magneto-resistance in manganites. Since (i) in many cases, materials with fundamentally new properties are found outside the chemical neighborhood of the "usual suspects" materials, and (ii) the development of accidentally-discovered materials may take a long time (because it takes a long time to figure out what it is that has been discovered), the current practice of materials-by-discovery may not be the best way to lead to game-changing technologies. We will prefer materials design over materials discovery. As far as theory is concerned, our strategy is to reverse the conventional approach of "given the structure of a solid or molecule, predict its electronic properties", into "given the target electronic properties (required for a given technological application), find the structure that has such properties" (Fig.1).

Fig. 1. Inverse-Design approach versus conventional approach to materials discovery.

The vision of "Inverse Design" could change the basic approach to materials research and potentially usher in a new era of materials science .To accomplish this vision we will conduct three steps.

First, we will articulate a set of desired, physical target properties. For optoelectronic semiconductors the target properties might be, for example, a given value of the band gap and effective masses, the ability to dope a material *p*-type or *n*-type, or a certain thermoelectric (ZT) response. For ferromagnets, the target might be a desired Curie temperature; for impurities in solids or surface states this might be a certain energetic position of the gap levels with respect to the band edges; for quantum dots a target might be a certain Auger recombination or exciton–multiplication rates. One might start by certain, broad classes of solids/alloys/nanostructures, initially selected on the basis of "Design Principles", which determine rather broad classes of materials (e.g, containing 10^6-10^8 individual compounds) likely to encompass the required target properties. The initial selection might be done on the basis of physical mechanisms that have been identified in past theoretical or experimental research.

Second, we will identify, via theoretical search of the above noted astronomic spaces of structures, the sub-class of atomic configurations whose electronic properties are close to the target property. This will be done e.g, using genetic or other biologically-inspired search algorithms in conjunction with quantum-mechanical calculations of the electronic structure. For example, for optoelectronic semiconductors we might find the atomic short-range or long-range order in a multi-component alloy that has given band gap or effective-masses; for magnetic ions in insulators we might find their spatial arrangement that has a given Curie temperature. Preliminary examples include (i) *Band gap design in superlattices:* A. Franceschetti and A. Zunger, Nature 402, 60 (1999); (ii) *Impurity design in insulators:* S.V. Dudiy and A. Zunger, Phys. Rev. Lett. 97, 046401 (2006); (iii) *Design of Curie temperatures in ferromagnets:* A. Franceschetti, S.V. Dudiy, S.V. Barabash, A. Zunger, J. Xu, and M. van Schilfgaarde, Phys. Rev. Lett. 97, 047202 (2007); and (iv) *Design of optical transitions and strain in nanostructures:* P. Piquini, P.A. Graf, and A. Zunger, Phys. Rev. Lett. 100, 186403 (2008).

Third, having narrowed down the range of candidate structures and materials from an initial astronomic number to a hopefully manageable range, we will employ both combinatorial synthesis and targeted synthesis, followed by material characterization, studying the material systems that fulfill the target properties. We envision the second and third steps to involve an iterative process between experiment and theory, whereby theoretically proposed structures are scrutinized by experiment and experimentally obtained feedback is used by theory to refine and further narrow the search of new materials.

The Inverse Materials Design Methodology integrates and combines all three components of Theory (prediction), Synthesis (realization), and Characterization (validation). The result will be orders of magnitude acceleration in the development of new materials. The general research concept for Inverse Design of materials is illustrated in Fig. 2:

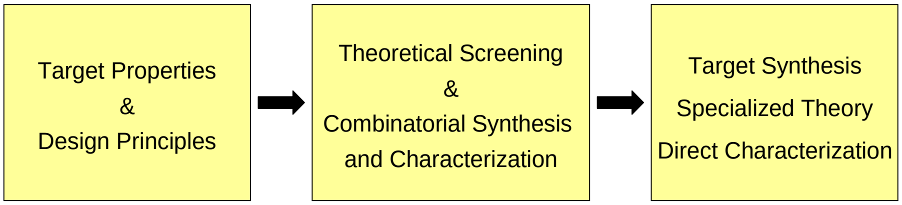

Fig. 2. The three components of the Inverse-Design approach.

We think that this philosophy is applicable to broad type of material properties (magnetism, ferroelectricity, superconductivity, transparent-conductors, to name a few) and to a broad range of structures (solids, alloys, polymers, molecular structures). The center will attempt to develop general methodologies that will be tested on specific cases, but will hopefully open the door for much broader applications in the future.

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Solar Fuels and Next Generation Photovoltaics
EFRC Director: Thomas J. Meyer
Lead Institution: University of North Carolina at Chapel Hill

Mission Statement: We will c*ombine the best features of academic and translational research to study light/matter interactions and chemical processes for the efficient collection, transfer, and conversion of solar energy into chemical fuels.*

Research in the UNC-EFRC will focus on three distinct areas selected to take full advantage of UNC-EFRC skills and address high priority Grand Challenge needs. The research groups representing the first two thrust areas will seek new strategies for the production of Solar Fuels and development of Photovoltaic technology. The Advanced Spectroscopy and Theory group will develop a new generation of experimental and theoretical methods needed to characterize physical properties and measure and understand functional performance of new materials and devices.

***A. Solar Fuels**:* Research in Solar Fuels will integrate light absorption and electron transfer driven catalysis in molecular assemblies and composite materials to create efficient devices for solar fuels; splitting water into hydrogen and oxygen and reducing CO_2 to hydrocarbons. Primary goals will be the discovery of new catalytic systems, the integration of structures, and the elucidation of mechanisms via cutting edge experimental and theoretical methods. Our work will proceed along two parallel lines:

(i) *Inorganic Materials*: In one area, efficient water splitting with solar energy will be pursued using high performance semiconducting nanomaterials and hierarchically assembled nanostructures. This will require designing new inorganic nanomaterials and molecular antennae to enhance light absorption, and new catalysts and architectures to achieve efficient proton reduction and water oxidation. Specific goals include: (1) prepare new semiconducting nanomaterials using flux synthetic methods; (2) develop new inorganic-organic hybrid materials with enhanced light absorption and tunable bandgaps; (3) explore and develop new forms of TiO_2 (nanotubes, nanosheets, etc.) for photocatalytic water splitting; and (4) synthesize catalysts for practical and efficient catalysis of water splitting and CO_2 reduction.

(ii) *Molecular Assemblies*: In a second area, efficient devices will be created with integrated molecular assemblies that use solar energy for solar fuel production; splitting water into H_2 and O_2 or water reduction of CO_2 to methanol or hydrocarbons. Specific goals include: (1) design and evaluate improved catalysts for electron transfer driven water oxidation and CO_2 reduction; (2) integrate solar fuel catalysts into molecular assemblies and composite materials that combine light absorption, vectorial electron transfer, and single electron transfer activation of multiple electron catalysis for fuel forming reactions; and (3) design and construct prototype devices for practical solar fuels production *via* photocatalytic water splitting and CO_2 reduction.

***B. Photovoltaics**:* Research in next-generation photovoltaics will focus on structurally preformed molecular assemblies and composites, with emphasis placed on the fundamental processes (e.g. energy transport, charge separation, etc.) that are common to solar fuels and photovoltaic technologies. Significant objectives will include synthesis of new assembly architectures, the measurement and analysis of exciton dynamics and energy and charge transport through complex materials, and development of patterned electrodes for light capture.

(i) Molecular Assemblies: Specific goals are to design and evaluate functional molecular assemblies that perform the complex steps needed for photovoltaic solar energy conversion. The group will: (1) design coiled-coil polypeptide assemblies that can precisely

position molecular sub-units in three dimensions; (2) develop methodologies for preparing assemblies with well-defined structures based on polypeptide and polymer architectures; and (3) design light-harvesting assemblies based on one-dimensional polymers that absorb sunlight and efficiently transport the excited state energy over long distances.

(ii) *Patterned Electrodes for Photonic Light Capture*: Specific goals include the use of printing technology to design, fabricate and test nanostructured metal-oxide electrodes for improved light capture in photovoltaic and solar fuels devices.

***C. Advanced Spectroscopy and Theory**:* The primary goal will be to develop the next generation of experimental and theoretical methods needed to analyze and explain the underlying phenomena that underpin solar energy science. Specific goals include:

(i) Develop experimental and theoretical methods for probing energy and charge transport in nanoscale materials: Experiment and theory will be combined to correlate charge and energy transport properties of materials with their underlying molecular architecture. Specific objectives include: (1) the use of ultrafast absorption and emission methods to follow energy and charge-transport through well-defined complex polymer and polypeptide systems; (2) the development of new theoretical models for simulating the movement of energy and charge in molecular, meso-, and macro-scale objects on femtosecond to microsecond time-scales; (3) the investigation of mechanisms for exciton generation, migration and dissociation, and charge transport in hybrid cells; and (4) the study of energy migration and carrier transport across nanostructured materials.

(ii) Ultrafast Spectroscopy of Molecular Excited States: New spectroscopic methods are needed to follow and analyze excited state dynamics in complex materials. The heterogeneous nature of these systems limits the utility of traditional linear spectroscopies and points to the need for new nonlinear spectroscopic methods. Specific objectives include the development of (1) femtosecond Raman spectroscopies sensitive to photoinduced electron transfer reactions, and (2) "multiplex" femtosecond ensemble experiments capable of correlating multiple exciton relaxation dynamics with particular members of a heterogeneous distribution.

(iii) Experimental and Theoretical Characterization of Catalytic Systems: The catalytic systems developed by the Solar Fuels groups will studied using a variety of state-of-the art experimental and theoretical tools. Specific objectives will include the determination of structure and the elucidation of mechanisms of homogeneous and heterogeneous catalytic systems.

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Non-equilibrium Energy Research Center (NERC)
EFRC Director: Bartosz A. Grzybowski
Lead Institution: Northwestern University

Mission Statement: To understand self-organization far from equilibrium and to use this knowledge to synthesize adaptive, reconfigurable materials for energy storage and transduction.

By closely interlinked synthesis, measurement, and modeling, the members of the NERC will explore the relationship between design, energetics, and far-from-equilibrium behavior in a number of significant materials systems. Our overreaching goal is to combine the theory of such systems with cutting edge nanotechnology and/or self-assembly to synthesize, characterize and understand in quantitative detail fundamentally new classes of materials that, while structurally robust, will have the ability to change and optimize their own performance (in energy processing, catalytic activity, etc.) in response to external/environmental stimuli. Creation of such "adaptive" materials that operate and/or maintain themselves away from thermodynamic equilibrium has the potential to revolutionize materials science and shift its focus from "static," equilibrium structures to "dynamic," multi-purpose materials. The Center will be built around a core (a "Think Tank") of expert theorists that interact closely with experimentalists working in five carefully selected "Focus Areas" combining the fundamentals of non-equilibrium research with the practice and applications of energy-related material systems. Specific experimental targets will include situations such as extension minima in rotaxane-based artificial muscles, controlling reaction networks by real-time catalytic switching, directing energy flows in orthogonal directions in multi-component quantum dot arrays, controlled molecular quantum transport in rigid rod-like assemblies of nanoscale plasmonic electrodes, and systems of power-generating, autnonomous "nanomovers".

We will focus on hard, soft, and hybrid materials. Theory, modeling and simulation efforts, fully integrated with synthesis and characterization, will include such approaches as phase-space characteristics and force-dissipation gradients in non-equilibrium systems, non-equilibrium Green's functions for electron transport studies, classical electrodynamics for plasmon behaviors, integrated atomistic, molecular, and coarse-grained molecular dynamics and related methods for extended length and time scale simulations, cluster-move Monte Carlo and agent-based algorithms for predicting non-equilibrium nanoscale assembly, transition path sampling and related methods to study morphological transitions, and classical density functional theory for self-consistent analysis of phase behaviors.

The three chief **goals** of this research are:

1. Significant fundamental insights into the nature of far-from equilibrium kinetics, dynamics, and structure formation for both quantum and classical systems.

2. A robust set of well-characterized, well-modeled physical systems in which far-from-equilibrium behaviors can be used to capture, transduce, store, and utilize many forms of energy.

3. A diverse group of graduates (undergraduate, doctoral, and postdoctoral) proficient in the preparation, measurement, and conceptual understanding of far-from-equilibrium systems. These graduates will be a central part of the human resources that the US requires to build a secure energy future based on understanding and creating new materials.

Non-equilibrium Energy Research Center (NERC)	
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Argonne-Northwestern Solar Energy Research (ANSER) Center
EFRC Director: Michael R. Wasielewski
Lead Institution: Northwestern University

The mission of the ANSER Center is to revolutionize our understanding of molecules, materials and methods necessary to create dramatically more efficient technologies for solar fuels and electricity production. The ANSER Center will achieve this vision by understanding and characterizing the basic phenomena of solar energy conversion dynamics, by designing and synthesizing new nanoscale architectures reconfigurable materials with extraordinary functionality, and by linking basic solar energy conversion phenomena across time and space to create emergent energy conversion systems operating with exceptional performance. At the same time, the ANSER Center seeks to create and mentor a technically excellent workforce capable of solving energy-related problems far into the future. To achieve these goals, ANSER Center objectives are to develop a fundamental understanding of:

- the interaction of light and charge with molecules and materials
- the energy levels and electronic structures of molecules and materials
- the dynamics of photoinduced charge generation, separation, and transport with unparalleled temporal and spatial resolution
- the interfaces at which charge generation, separation, transport, and selective chemical reactions occur
- the properties of unique materials, from self-assembling, bio-inspired materials for hydrogen fuel production from water to transparent conductors and nanostructured hard and soft materials for solar electricity generation.

Subtask 1: Bio-inspired molecular materials for solar fuels. Natural photosynthesis is carried out by assemblies of photofunctional chromophores and catalysts within proteins, which provide specifically tailored nano-environments to optimize solar energy conversion. Achieving integrated artificial photosynthetic systems requires hierarchical organization at both molecular and supramolecular levels to capture light energy, separate charge, and transport charge to catalytic sites at which fuel synthesis occurs, e.g., H_2O oxidation to generate H_2. We do not yet understand in detail the basic scientific principles needed to build self-ordering, self-assembling components or the tailored nano-environments necessary to realize efficient, integrated artificial photosynthetic systems. The goals of Subtask 1 are to:

- Discover and utilize the fundamental scientific principles necessary to self-assemble biomimetic molecular systems to harvest light and perform photochemical charge separation.
- Discover and utilize the fundamental scientific principles necessary to couple photogenerated charges to multi-electron, multi-metallic catalysts for H_2O oxidation and H^+ reduction to H_2.
- Develop and utilize the fundamental understanding of how supramolecular assemblies and modified photosynthetic proteins can provide the tailored nano-environments necessary produce an integrated artificial photosynthetic system (e.g. Fig. 1).

Subtask 2: Interface science of organic photovoltaics. Organic photovoltaics (OPVs) offer the promise of low-cost, readily manufacturable alternatives to traditional inorganic systems for producing solar electricity. Power conversion efficiencies as high as 10-12% may be achievable, if crucial scientific understanding challenges can be surmounted. Progress requires

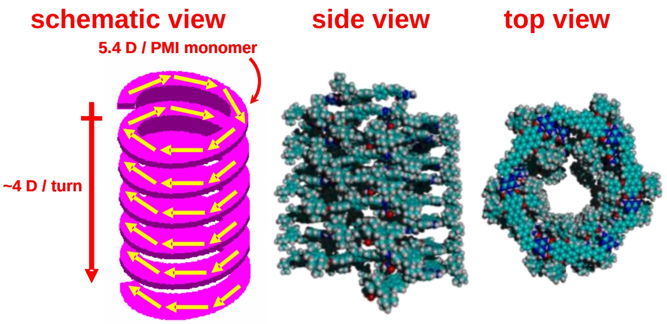

Fig. 1. Self-assembling nano-environment for integrated artificial photosynthesis.

a highly collaborative group, with experts in transparent conducting oxides (TCOs), in tailoring their interfaces with soft matter, in supramolecular assembly of charge-transporting arrays, and in applying an arsenal of state-of-the-art physical characterization and theoretical techniques. Subtask 2 combines unique, complementary expertise and resources, attacking key problems in OPV interface science in a comprehensive, integrated fashion, to achieve prototype cells which test enabling new concepts (e.g. Fig. 2). The resulting knowledge, materials, and techniques will be exploited in other types of interfaces necessary to implement the photodriven catalysts and solar cells in Subtasks 1 and 3, respectively.

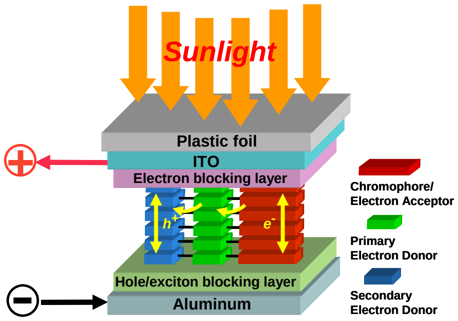

Fig. 2. A multilayer organic solar cell.

Subtask 3: Nanostructured architectures for photovoltaic and photochemical energy conversion. This subtask will define, develop, model, and test robust new nanostructured architectures, and associated new synthetic methodologies, that promise to advance substantially the science and technology of photovoltaic and photochemical solar energy conversion. Specifically, the subtask will focus on high surface area inorganic architectures capable of addressing key challenges in the design of exceptionally efficient Dye Sensitized Solar Cells (DSSCs) and highly functional fuel-producing solar cells (Subtask 1). This work will build on many of the activities in Subtasks 1 and 2 and synergistically provide information back to these subtasks. Dye-sensitized solar cells (DSSCs) represent one of the most promising alternatives to expensive silicon technology for conversion of solar radiation to electricity (Fig. 3a). Specifically, we will use new materials synthesis techniques to create conducting, semiconducting, and insulating oxide and metal nanostructures that can be used to systematically control key electronic, catalytic, and optical phenomena, and to favorably manipulate device dynamics and energetics. These structures will enable the plasmonic amplification of light harvesting ability, the use of energetically optimized redox shuttles that do not work in conventional architectures, and the coupling of photoelectrodes to fuel-forming catalysts (Fig. 3b).

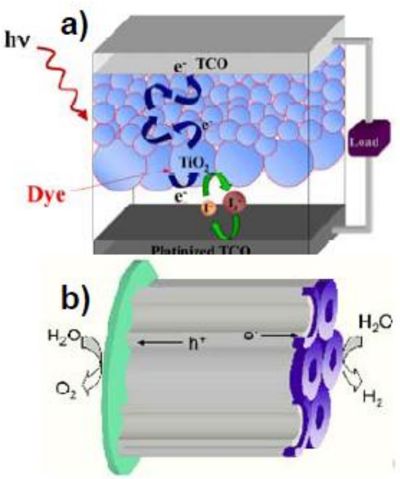

Fig. 3. a) DSSC based on electron injection into a wide bandgap, nanocrystalline, n-type semiconductor medium. **b)** *Compartmentalized* light-harvesting, catalytic oxidation, and catalytic reduction components function on a high-area, high-porosity, electrically conductive platform.

Argonne-Northwestern Solar Energy Research (ANSER) Center	
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Materials Science of Actinides
EFRC Director: Peter C. Burns
Lead Institution: University of Notre Dame

Mission Statement: The mission of the Materials Science of Actinides (MSA) EFRC is to conduct transformative research in the actinide sciences with full integration of experimental and computational approaches, and an emphasis on research questions that are important to the energy future of the nation. Workforce development is a motivating goal of this university-based center.

The *Materials Science of Actinides* Center unites researchers from five universities and three national laboratories to conduct transformative research in actinide materials science. Actinides are, in many ways, at the frontier of exploration of the periodic table, as their chemistry is complicated by the importance of the 5*f* electrons, relativistic effects, and their complex redox chemistry. Owing to this complexity and the relative difficulty of working with actinides, research in actinide chemistry and actinide-based materials has lagged far behind that of most other elements in the periodic table, both in theory and synthesis and design for special properties, such as radiation resistance of actinide-bearing materials.

In actinides, the delocalization/localization of 5*f* electrons presents the possibility of control of materials processes at the level of electrons. Indeed these properties emerge from the complex correlations of atomic (composition and short and long-range order) and electronic (*f*-electron) constituents. In this center, we will heavily emphasize new synthesis approaches for actinide materials that are likely to lead to revolutionary new forms of matter with tailored properties. New materials that we emphasize are based upon the self-assembly of actinides into nanoscale materials with the potential to create new technologies. Radiation in actinide materials creates a system that is very far away from equilibrium, and a core focus of this center is to examine the behavior of actinide-based materials under extreme conditions of radiation, pressure and temperature.

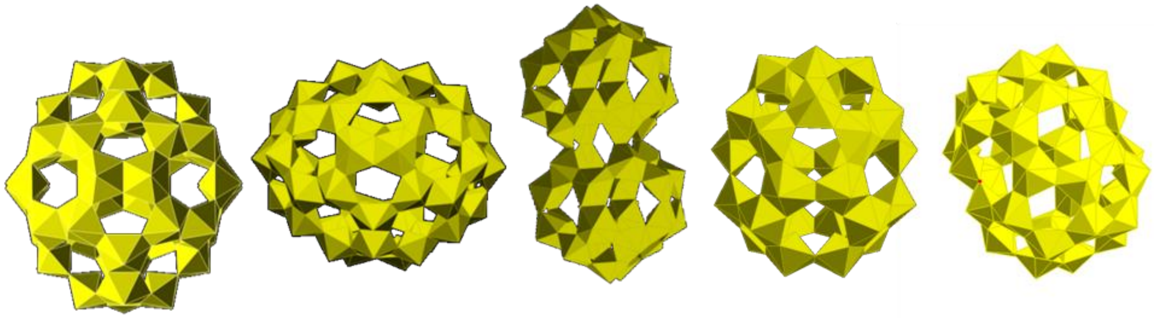
Three major Research Themes in actinide materials science are central to MSA's efforts. These themes are: Complex actinide materials, Nanoscale actinide materials, and Actinide materials under extreme environments. Four cross-cutting themes are: Actinide behavior at the nanoscale, Thermochemistry of actinide materials, Synthesis of new types of actinide materials, and Modeling of actinide materials.

The complex actinide materials theme includes the synthesis and properties of fluorite-structured materials with tetravalent actinides in solid solution, as well as the effects of extreme environments on such materials. It also encompasses the complex structural topologies typical of the higher-valence actinides, and details of the hydrothermal reactions used in synthesis of such materials.

The nanoscale actinide materials theme focuses on the self-assembly of actinide-centered polyhedra into complex clusters (see figure below). This research combines synthesis, synchrotron studies, computations, and thermodynamics to gain insights into the formation mechanisms, stability fields, and bonding requirements of such clusters.

The actinide materials under extreme environments theme examines the many phenomena in actinide solids that are temperature and/or pressure dependent – such as, order-disorder transformations, other phase transitions, and chemical decomposition. The coupling effects of extreme temperature and pressure environments with strong radiation fields are emphasized.

Our research will make essential use of DOE-BES and DOE-BER user facilities including, but not limited to, the Advanced Photon Source (APS) at Argonne National Laboratory (ANL), the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL), the Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National Laboratory (PNNL), the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), and the IVEM-Tandem Facility at ANL (as well as international facilities where comparable facilities do not exist in the U.S.).



Nanoscale uranyl peroxide clusters synthesized and structurally chracterized. Each cluster is built from uranyl hexagonal bipyramidal polyhedra. These clusters, which contain as many as 60 uranium atoms, self-assemble in alkaline solutions under ambient conditions.

Materials Science of Actinides (MSA)	
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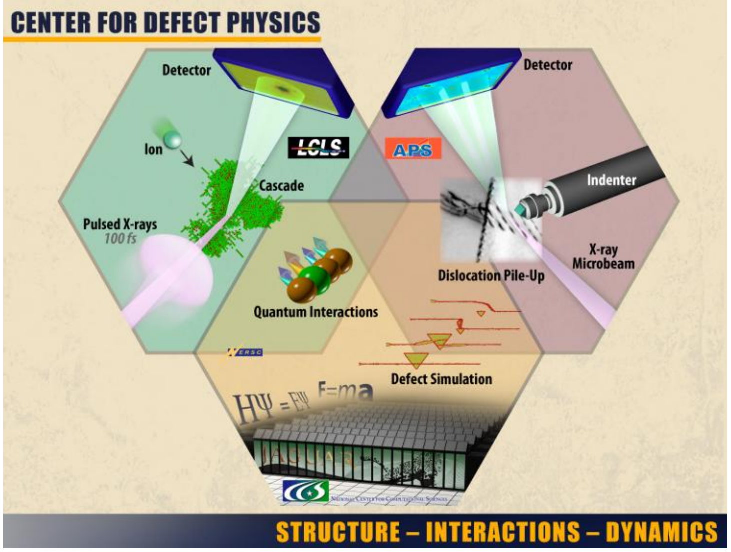
Center for Defect Physics in Structural Materials (CDP)
EFRC Director: G. Malcolm Stocks
Lead Institution: Oak Ridge National Laboratory

Mission Statement: To provide a fundamental understanding of materials' defects, defect interactions, and defect dynamics, thereby enabling atomistic control and manipulation of defects and the charting of new pathways to the development of improved materials – materials with ultra-high strength, toughness, and radiation resistance.

The *"Energy Frontier Center for Defect Physics in Structural Materials (CDP),* focuses on providing the fundamental knowledge to allow atomistic control and manipulation of defects, defect interactions, and defect dynamics – the very defect properties that currently limit the performance and lifetime of materials. Under-pinning the CDP is the realization that we are on the verge of a new era of *quantitative measurement* and *direct quantum simulation* of the dramatic impact of defects on bulk structural materials. Further-more, that the new era can be realized by utilizing innovative experimental techniques and major national facilities, such as the Advanced Photon Source (APS) and the Linac Coherent Light Source (LCLS), and by advancing the frontiers of first principles simulations using the, soon to be PFlop/s computing power available at the National Center for Computational Science (NCCS) and the National Energy Research Scientific Computing Center (NERSC).



Schematic of the key elements of the CDP highlighting the links between the three research thrusts and the use of major DOE user-facilities to study defects and the unit events that ultimately control materials response to extremes of stress and irradiation.

The overarching goal of the CDP is to bring a radically new level of rigor and insight to the discussion of defect structure, interactions, and dynamics in metals and alloys – rigor born of quantitative experimental studies of defect evolution at the level of unit defect events and insight born of highly accurate calculations and simulations of properties that are based on a full quantum description of the underlying electronic interactions. The Center focuses on three interrelated research thrusts (RT) areas:

<u>RT1: *Fundamental Physics of Defect Formation and Evolution during Irradiation*</u>: Research in this thrust addresses one of the most fundamental and challenging issues in radiation damage through direct measurement of the dynamics of atomic displacement cascades. The underlying science of the formation and evolution of energetic-ion induced atomic displacement cascades as unit events will be probed for the first time using ultra-high resolution time-resolved x-ray diffuse scattering measurements. Measurements ranging from the sub-picosecond generation through millisecond range evolution of cascades will exploit the ultra-high brilliance of femtosecond x-ray pulses that will be produced by the LCLS. Together with complementary damage accumulation investigations and the development of first-principles-based molecular dynamics techniques in RT3, a multi-pronged approach will

be directed toward a full understanding of the generation, accumulation, and the potential for mitigating radiation damage in structural materials.

<u>RT2: *Fundamental Physics of Defect Interactions during Deformation*</u>: Research in this thrust addresses fundamental and longstanding issues associated with achieving a quantitative understanding of the local stresses near single dislocations, their aggregates, and the stress-driven interactions of dislocations with microstructural features (e.g. grain-boundary pile-ups). Recently developed submicron-resolution 3D x-ray microscopy at the APS will be used for groundbreaking non-destructive measurements of the local stresses and the indenter-driven motion and interactions of single dislocations as fundamental unit events of deformation in bulk and micro-pillar metals and alloys. Complementary investigations of the local stresses that drive dislocation motion and interactions with irradiation-induced defects will be performed in connection with RT1, and all measurements will be performed in close synergy with top-down and first-principles-based theory and simulations in RT3.

<u>RT3: *Quantum Theory of Defects and Interactions*:</u> Research in this thrust will overcome limitations of DFT molecular dynamics with respect to accuracy, system size, and simulation time by advancing the underlying theory and the software implementation of the theory on high performance computers. Consistent with the experimental challenge of quantifying the unit events of defect formation, evolution, and deformation, the modeling task will develop high fidelity models treating spin and ion dynamics on an equal footing and addressing system sizes and time scales commensurate with experiments in RT1 and RT2. Using comparisons with essentially exact quantum Monte Carlo calculations for magnetic systems to ensure accuracy as new DFT functions are developed, intelligent use of the raw computing power of the NCCS and NERSC facilities will be supplemented by classical ion-spin dynamics and diffusive atom density MD to go beyond the state of the art, e.g. in the inclusion of spin degrees of freedom.

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Fluid Interface Reactions, Structures and Transport (FIRST) Center
EFRC Director: David J. Wesolowski
Lead Institution: Oak Ridge National Laboratory

The FIRST Center will develop predictive computational models relating the nanoscale structures dynamics and reactivities of fluid-solid interfaces in order to make transformational advances in electrical energy storage and catalysis for energy applications.

The overarching goal of the FIRST Energy Frontier Research Center is to address the fundamental gaps in our current understanding of interfacial systems of high importance to future energy technologies, including electrical energy storage (batteries, supercapacitors) and heterogeneous catalysis for solar energyand solar fuels production. The FIRST Center will address three key questions:

- How does the interfacial region differ in structure, dynamics and reactivity from the bulk properties of the fluid and solid phases?
- How do these altered properties couple with complex interfacial textures to influence chemical reactions, ionic and molecular transport and charge transfer within and across the interface?
- How can we control interfacial phenomena by informed design of fluid- and solid-phase components, interfacial geometries, field gradients and environmental parameters?

These questions permeate the fundamental science needed to solve our nation's long-term energy production, storage and utilization needs, as described in the DOE/BES Basic Research Needs Workshop and Grand Challenge reports. The interaction of fluids with solid substrates controls many chemical processes encountered in nature and industry. However, the atomic-nanoscale structures, reactivities and transport properties of the fluid-solid interface (FSI) are poorly understood for the vast majority of fluid-substrate combinations, particularly at environmental extremes (e.g., high surface charge density, extreme chemical non-equilibrium, high ion/electron fluxes, etc.). This lack of fundamental molecular-level understanding of interfacial phenomena has often lead to Edisonian approaches to the resolution of challenges related to advanced energy technologies, including solar energy utilization, energy storage (batteries and supercapacitors), heterogeneous catalysis, and chemical separations. To address these challenges, we must replace continuum solvent descriptions and hypothetical interfacial structures, with *quantitative, fully dynamic, and chemically realistic descriptions of the interactions of electrons, atoms, ions and molecules that give rise to macroscopic interfacial properties.* The First Center will bring together a multidisciplinary, multi-institutional team of scientists, postdoctoral associates and students to redefine the FSI and enable predictive understanding and control of interfacial processes.

Unique FSI properties emerge from a complex interplay of short- and long-range forces and reactions among the molecular fluid components, solutes and substrates. Potential gradients (chemical, electrical, etc.) can be highly non-linear at the angstrom-nanometer scale. The finite size, shape, directional bonding, charge distribution and polarizability of solvent and solute components are convoluted with their ability to reorient, 'unmix' and react with one another and the substrate. The truncated solid surface exposes under-bonded atoms that drive dynamic interactions with the adjacent fluid by local bond relaxation, charge redistribution, dissolution, precipitation, sorption and porosity development/destruction. We intend to replace static, hypothetical, continuum models with what we will refer to as "FSI models" that capture the atomic-molecular-nanoscale structural, reactive and transport properties of real interfaces, over the relevant time (femtosecond-millisecond) and length (sub-angstrom to sub-micron) scales of interfacial systems. *This will provide an unprecedented level of understanding, predictability and* *control of interfacial transport and reactivity, and provide guidance for the design of new materials with extraordinary properties to address our future energy needs.*

Our strategy is to take a hierarchical and highly-integrated approach, coupling unique experimental, chemical imaging, materials synthesis and computational approaches to probe FSI structures, reactions, and transport phenomena. In Thrust 1, we will investigate polar organic and ionic liquid interactions with charged and uncharged carbon surfaces in a planar or unconfined geometry. This will enable the application of advanced neutron, X-ray, NMR and nonlinear optical probes of interfacial structure and dynamics and will facilitate coupling these atomic-nanoscale imaging results with multiscale computational models that capture the chemical realism of interfaces. In Thrust 2, we will extend these approaches to determine how nanoscale confinement, surface roughness, functionalization and alteration due to chemical reactions with the fluid influence solvent/solute transport at uniquely-tailored carbon surfaces and with novel electrolyte structures and chemistries. In Thrust 3, we will determine how the unique properties of interfacial fluids couple with catalysts and substrates to control reaction pathways, selectivity, and energetics of proton-coupled electron transfer reactions involving CO_2 and O_2. The research will be mainly conducted at Oak Ridge National Laboratory (ORNL), with extensive activities at our partner institutions, Vanderbilt, Drexel and Northwestern Universities, Argonne National Laboratory (ANL) and the University of Virginia. Much of the key research will be conducted in major DOE/BES user facilities, including ORNL's Spallation Neutron Source/High Flux Isotope Reactor (SNS/HFIR), National Center for Computational Sciences (NCCS) and Center for Nanophase Materials Sciences (CNMS), as well as ANL's Advanced Photon Source (APS).

The three research thrusts will be pursued in parallel, but will involve intensive integration of effort and involvement of the same team members across the thrusts. The goal of these thrusts is to develop FSI models that capture the actual structures, compositions and solute-solvent-substrate interactions that control interfacial properties, reactivity and transport. The level of computational rigor and molecular-level detail incorporated into the FSI models will vary from one thrust to another, as the systems increase in complexity. These models will also evolve through integration among the thrusts, and breakthroughs in computational and experimental capabilities in this program and throughout the scientific community. We fully intend to modify our targets and approaches judiciously, as these new opportunities arise. An intensive effort to share our results with the broader scientific community and to engage experts from across the energy technology landscape will keep the FIRST Center at the forefront of interfacial science and offer a rich environment in which to train the next generation of scientists to meet 21st century energy challenges.

Fluid Interface Reactions, Structures and Transport (FIRST) Center	
Oak Ridge National Laboratory	**David J. Wesolowski (Director)**, G.M. Brown, A.A. Chialvo, D.R. Cole, S. Dai, N.J. Dudney, E.W. Hagaman, D. Jiang, P.R. Kent, K.L. More, S.H. Overbury, G. Rother, R.W. Shaw, Z. Wu
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The Center for Molecular Electrocatalysis
EFRC Director: R. Morris Bullock
Lead Institution: Pacific Northwest National Laboratory

Mission Statement: We seek to understand, predict, and control the intra- and intermolecular flow of protons in electrocatalytic multi-proton, multi-electron processes of critical importance to a wide range of energy transformation reactions, including production of H_2, oxidation of H_2, reduction of O_2, and reduction of N_2, by studying how proton relays regulate the movement of protons and electrons within and between molecules to enhance rates of electrocatalysis.

Electrocatalysts that efficiently convert electrical energy into chemical bonds in fuels, or the reverse, converting chemical energy to electrical energy, will play a vital role in future energy storage and energy delivery systems. Electrocatalytic processes involving multi-proton and multi-electron redox reactions are pervasive in energy science. The Center for Molecular Electrocatalysis will address fundamental challenges in understanding how molecular electrocatalysts function, and will use this knowledge to rationally design new classes of molecular electrocatalysts for important energy storage and utilization reactions. Closely coupled experimental and theoretical studies will include inorganic synthesis, ligand design, mechanistic studies, electrochemical measurements, determination of thermochemical values for metal hydride complexes, and evaluation of catalytic activity.

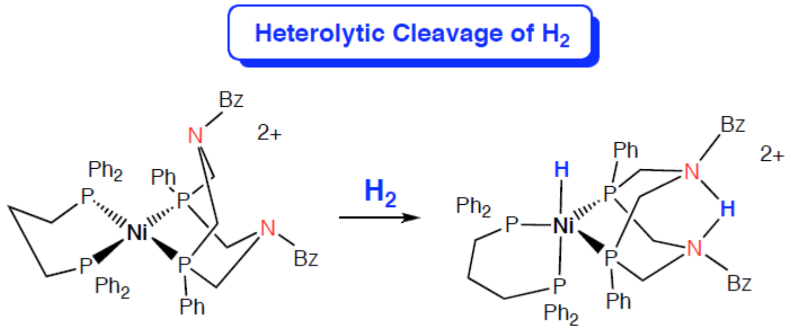
Electrocatalytic reactions to be studied include the production of hydrogen, oxidation of hydrogen, reduction of oxygen, and reduction of nitrogen. These critical reactions range from two-proton, two-electron processes to six-proton, six-electron reactions. A unique approach in this Center will be a focus on proton relays, which are functional groups (typically amine bases) that play a crucial role in the delivery of protons to (or from) the active site of molecular catalysts. Catalysts containing proton relays developed by researchers at PNNL exhibit activities for hydrogen production comparable to those of the NiFe hydrogenase enzymes used in Nature, far surpassing other synthetic catalysts. *The prevalence in energy science of reactions that require controlled movement of protons and electrons presages an immense scope for the roles of proton relays.*

The reduction of protons derived from water to form hydrogen is the simplest fuel generation reaction (eq. 1, forward direction). The reverse process, the oxidation of H_2, is an important reaction in hydrogen fuel cells. The four-electron reduction of O_2 to form water, (eq. 2, forward direction), is important in almost all currently used fuel cells, providing the reductive half-reaction to balance the oxidative half-reaction. The opposite process, (eq. 2, reverse direction), the four-electron oxidation of water to form O_2, is required for water splitting, and has been intensively studied in connection with solar energy utilization. Reduction of nitrogen to give ammonia (eq. 3, forward direction) is a six-electron process. This reaction is already of global importance; the Haber-Bosch process for conversion of nitrogen to ammonia consumes about 1% of the world's total energy supply, and contributes enormously to our ability to provide food for the world's growing population.

$$2\,H^{+} + 2\,e^{-} \rightleftharpoons H_2 \qquad (1)$$

$$O_2 + 4\,H^{+} + 4\,e^{-} \rightleftharpoons 2\,H_2O \qquad (2)$$

$$N_2 + 6\,H^{+} + 6\,e^{-} \rightleftharpoons 2\,NH_3 \qquad (3)$$



Molecular catalysts offer a degree of precise structural control – and therefore the precise probing of relationships between catalyst structure and activity – that are not possible for either heterogeneous catalysts or enzymes. *It is precisely this structure-activity knowledge that we are seeking to develop*. The two-, four-, and six-*electron* redox processes in eqs. 1-3 for H_2, O_2, and N_2, are also two-, four-, and six-*proton* processes. Facile and controlled movement of both electrons *and* protons from solution to substrates bound at the active metal site is essential for these electrocatalytic reactions. Proton transfers will need to be very carefully controlled and designed. The generality of proton transfer processes in almost all fuel generation and utilization reactions makes understanding these processes at a fundamental level of enormous importance.

Proton relays are functional groups that play a crucial role in the delivery of protons to (or from) the active site of catalysts. They are thought to play an important role in hydrogenase enzymes, the oxygen-evolving complex, and other biological systems.

Our goals at the Center for Molecular Electrocatalysis are to:

- Obtain a fundamental understanding of how proton relays accelerate proton transfers, both intra- and intermolecularly
- Understand how proton transfers can be coupled with electron transfers to accelerate catalytic reactions
- Demonstrate that a comprehensive understanding of proton relays can be used to design highly active molecular electrocatalysts for vital reactions required for a secure energy future.

Center for Molecular Electrocatalysis	
Pacific Northwest National Laboratory	**R. M. Bullock (Director)**, D. L. DuBois, M. Dupuis, R. Rousseau, C. Yonker, A. Appel, W. J. Shaw, J. C. Linehan
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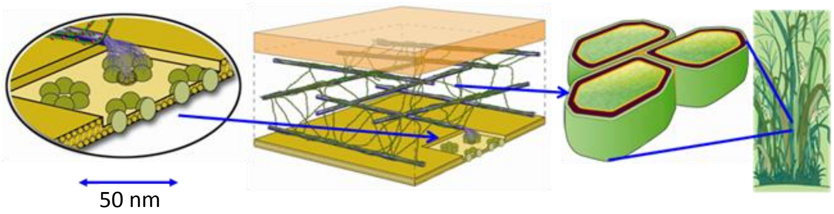
Center for Lignocellulose Structure and Formation (CLSF)
EFRC Director: Daniel Cosgrove
Lead Institution: Penn State University

Mission Statement: CLSF will develop a detailed understanding of the nano-scale structure of lignocellulose and the physico-chemical principles of its formation. Lignocellulose is the major structural material of plant bodies and constitutes the enormously important biorenewable resource used to make building materials, paper, textiles and many polymer derivatives. It is also largest available source of biomass on Earth with the potential for conversion to transportation fuels to replace petroleum. Despite its economic significance, many basic questions about its structure and formation are unanswered. This is the focus of the center. CLSF has 3 interrelated themes, illustrated at right.



Center theme 1: Understand Cellulose synthesis

Center theme 2: Understand Lignocellulose assembly

Center theme 3: Understand relationship between nano scale structure and macro scale properties

Theme 1 focuses on CSC, the Cellulose Synthase Complex, and the physical process of cellulose microfibril formation in plant and microbial systems. Specific objectives include:

CSC structure: Crystallize the catalytic core of Acs and Ces cellulose synthesis protein systems and develop a structural model; Analyze plant CSC from genetically engineered and/or mutant Arabidopsis lines; Work with modelers to incorporate all proven aspects of CSC structure and operation into their emerging models; Apply freeze fracture TEM to visualize the CSC and, possibly, sites of microfibril extrusion in protoplasts; and parallel work above for the bacterial CSC.

Nanoengineering: Reconstitute an active CS, using both Acs and plant CesA enzymes, into artificial membranes assembled within nanotube and nanomembrane arrays and demonstrate and manipulate CesA/CSC biochemical and biophysical function in a nano-engineered system. Use this nano-engineered platform to facilitate biophysical spectroscopic studies by providing macroscopic alignment for improved resolution, long-term sample stability, and feasibility of examination of the same sample by NMR, EPR, IR, fluorescence, etc. Refine structural models by combining experimental spectroscopic data with structural predictions of the computational modeling, and, in turn, refine the developed models.

Computational modeling: Predict secondary and three-dimensional structure of an individual CesA protein. Build a prototype computer model of CesA packing within the CSC. Explore the packing of predicted transmembrane helices in a membrane using multiscale molecular dynamics modeling. Predict the structure of the "rosette" using molecular mechanics simulations. Model the structure of crystalline cellulose and how crystallization occurs.

Theme 2 focuses on the structure and assembly of lignocellulose from its constituent components (cellulose, hemicellulose, lignin). Objectives include:

Binding and assembly studies: Characterize the dynamics and energetics of specific cellulose-polysaccharide-protein-enzyme-lignin binding interactions using isothermal titration calorimetry (ITC) and surface plasmon resonance techniques. Explore the dependence of binding parameters on the form of cellulose and the details of xyloglucan, arabinoxylan and lignin structure. Proteins and enzymes include expansins, and related nonenzymatic proteins that alter cell wall rheology, and cellulases. Combine data with molecular modeling results to understand the key molecular elements of cellulose-matrix binding interactions. Correlate self-assembly and binding with structure enabling further correlations with results from ITC, vibrational spectroscopy, and computational modeling.

Model systems for 3D assembly studies: Develop model three dimensional synthetic plant cell wall systems implementing aligned cellulose fibrils in a flow cell. Introduce compounds such as hemicelluloses, lignins, pectins, etc., into the chamber and assess the impact on assembly. Develop a plant protoplast model system for studying the initial stages of cellulose synthesis, cellulose structure, and cell wall polymerization in Arabidopsis and *Populus* cells. Control the crystallinity of cellulose through genetic modification to significantly improve the enzymatic digestibility of cellulose. Identify novel cellulose structure in *Acetobacter xylinum* mutants through genetic modification and culture conditions. Perform computational modeling of interactions and assembly.

Spectroscopy and scanning probe microscopy studies: Elucidate cellulose-carbohydrate interactions with experimental and computational IR using models generated by the center to address such issues as whether or not the carbohydrate binds crystalline or amorphous domains. Experimentally study the effect of lignin type (degree of branching, molecule size, etc.) and reactant sequence on the solubility of xylan in cellulose-xylan-lignin complexes. Perform batch syntheses of collections of biomimetic cell wall complexes that can be recovered for further evaluation of how chemistry and microstructure relate to macroscopic properties. Explore the use of atomic force acoustic microscopy for analyzing cell wall mechanical properties and their dependence on cell wall structure and the modification by expansins, xylanases and other cell wall-loosening enzymes.

Theme 3 focuses on the development and validation of a multiscale model that will bridge the basic nano and molecular scale knowledge gathered in themes 1 and 2 to real-world applications including drying and chemical/enzymatic degradation. The following are specific objectives:

Nanoscale characterization and modeling of cell wall structure: Quantify cell wall composition (cellulose, hemicellulose, lignin, and pectin) of model and natural plant materials in order to define components for multiscale modeling. Characterize macroscale thermal and mass transport properties of natural and model plant materials. Perform computational multiscale modeling with application to structural, mechanical, thermal and transport properties/processes. Characterize biomass degradation by enzymatic or chemical means under controlled conditions. Apply multiscale models to interpret the degradation processes as impacted by nanoscale lignocellulose structure; Extend atomistic modeling to larger length and time scales by use of a coarse-grained model which incorporates atomistic detail; Develope a coarse grained simulation model for cellulose structure and crystallization. Identify 4-5 model structures for study using small angle neutron scattering. Correlate cellulose crystallinity and fibril structure with material properties. Characterize interdiffusion of water and deuterated polysaccharides in interfacial regions using neutron reflectivity.

Center for Lignocellulose Structure and Formation	
Pennsylvania State University	**Daniel Cosgrove (Director)**, Jeffrey Catchmark (Associate Director), Tom Richard, James Kubicki, Ming Tien, Teh-hui Kao, Janna Maranas, John E. Carlson, Virendra Puri, Nicole Brown, Linghao Zhong, Douglas Archibald, Bernhard R. Tittmann, Vincent Crespi
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Combustion Energy Frontier Research Center
EFRC Director: Chung K. Law
Lead Institution: Princeton University

Mission Statement: To develop a validated, predictive, multi-scale combustion modeling capability for non-petroleum-based fuels, especially renewable biofuels, for transportation applications and for optimizing the design and operation of advanced engines using these fuels.

That there is an urgent need to develop renewable transportation fuels is abundantly substantiated by recent concerns over energy sustainability, energy security, and global warming. Predictive tools for relating the fuel constituent composition and operational characteristics of energy conversion systems are needed over the next few decades as the world transitions away from conventional, petroleum-derived transportation fuels. Empirical approaches to developing new engines and certifying new fuels have led to only incremental improvements, and as such they cannot meet future challenges in a timely, cost-effective manner. Achieving the required rate of innovation will depend strongly upon computer-aided design, as is currently used to design the aerodynamically efficient air frame of advanced commercial aircraft and the molecular composition of ozone-friendly refrigerants. The diversity of alternative fuels and the corresponding variation in their physical and chemical properties, coupled with simultaneous changes in the design/control strategies of energy conversion devices to improve efficiency and reduce emissions, pose immense technical challenges. These challenges are particularly daunting since energy conversion efficiencies and exhaust emissions are governed by coupled chemical and transport processes at multiple length scales ranging from the electronic structure of molecules to molecular interactions and rearrangements to nanoscale particulate formation to turbulent fuel/air mixing. Fortunately, recent advances in quantum chemistry, chemical kinetics, reactive flow simulation, scientific computation, and experimental flame diagnostics suggest that first-principles-based predictive tools for optimum integration of energy conversion and control methodologies and new fuel compositions are possible. Figure 1 shows the calculated turbulent flame structure of an ethylene-air jet flame using direct numerical simulation (DNS) and a realistic model of the chemistry. Parts of the experimental program of this EFRC will utilize the Advanced Light Source at the Lawrence Berkeley National Laboratory.

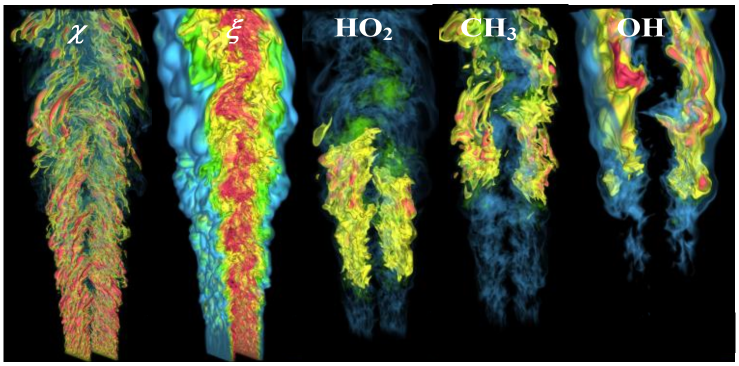

Figure 1: DNS of a lifted ethylene-air jet flame in a heated coflow at a Reynolds number of 10,000. Instantaneous volume rendering from left to right: scalar dissipation rate, mixture fraction, and mass fractions of HO_2, CH_3, and OH.

Motivated by the above challenges and opportunities, the goals of the Combustion-EFRC are the following:

1) To advance fundamental understanding and practice of combustion and fuel science. This includes the development of quantum mechanical methods for thermochemistry and kinetics at high pressures, the development of nonequilibrium transport models

and models of nanoscale particulate inception, growth and oxidation, and the discovery and modeling of new phenomena of near-limit laminar and turbulent combustion.

2) To create experimental validation platforms and databases for kinetics, thermochemistry, transport processes, and flame structure through application of advanced extractive and in situ diagnostic methods.
3) To enable automated kinetic model generation and reduction.
4) To implement validated, multi-scale, quantitative prediction methods for novel energy conversion design/control concepts tailored to physical and chemical properties of non-petroleum-based fuels.
5) To establish a knowledge highway connecting the EFRC, academic and research institutions, and the transportation and fuel industries.
6) To train the next generation of combustion scientists with the multi-disciplinary background needed to tackle these immensely challenging combustion energy problems.

The proposed research therefore directly addresses three of the BESAC Grand Challenges:

(a) Designing non-petroleum-based transportation fuels with fundamentally new structures and properties through the judicious manipulation of their molecular composition by controlling matter at the level of the electron and the atom.

(b) Controlling the reactions of these fuels to produce clean and efficient energy using advanced conversion devices requiring the characterization and control of matter far from equilibrium.

(c) Developing a multi-scale approach to characterize the emergent properties of new bulk fuels in terms of properties at successively smaller scales down to the atomic and electronic.

Combustion Energy Frontier Research Center (C-EFRC)	
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Cornell University	S.B. Pope
Massachusetts Institute of Technology	W.H. Green
Sandia National Laboratories	J.H. Chen, N. Hansen, J.A. Miller
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Center for direct Catalytic Conversion of Biomass to Biofuels (C3Bio)
EFRC Director: Maureen McCann
Lead Institution: Purdue University

***Mission Statement*:** C3Bio will develop transformational technologies that maximize the energy and carbon efficiencies of biofuel production by the rational and synergistic design of both physical and chemical conversion processes and the biomass itself.

Plants filter carbon dioxide from the atmosphere with very high efficiency, using solar energy to construct sugars and aromatic molecules that are stored in lignocellulosic biomass. A billion tons of lignocellulosic biomass is an annually renewable resource of home-grown energy available from U.S. agriculture and forestry. Second-generation biofuels will be derived from lignocellulosic biomass using biological catalysis to use the carbon in plant cell wall polysaccharides for ethanol or other biofuels. However, this scenario is both carbon- and energy-inefficient. The major components of biomass are polysaccharides and lignin, the latter accounting for ca. 25-30% by weight. First, biological conversion routes use only the polysaccharide moiety of the wall, hydrolyzing the polysaccharides to sugars as carbon sources for microbes. Second, the presence of the lignin interferes with the access of hydrolytic enzymes to the polysaccharides, thereby inhibiting their conversion to sugars. Third, the living micro-organisms, required to ferment the sugars to biofuels, utilize some sugars in their own growth and co-produce carbon dioxide at undesirable levels. In contrast, the power of chemical catalysis to transform biomass components to liquid biofuels and other useful molecules is an underexplored area of science that has tremendous potential impact on carbon and energy efficiencies. Restructuring biomass polysaccharides and lignin into energy-rich fuel molecules requires us to achieve a deep understanding of biomass-catalyst interactions, and at the atomic level, to provide a rational basis for design of optimized catalysts and biomass tailored for the end-use of catalytic conversion. We have three specific research thrusts:

Thrust 1. Apply new catalytic transformations to biomimetic structures and lignocellulosic biomass variants, and identify highly efficient process pathways. All cell wall components contain at least some oxygen and require the development of catalytic deoxygenation chemistry and selective bond breaking to enable efficient transformations of lignin and polysaccharides to useful products. First, we will investigate homogeneous catalysts in condensed phase starting with simple models of monomers and dimers and build up to more complex oligomeric, polymeric and macromolecular structures, native biomass, and finally, biomass that is genetically engineered to be optimized for catalytic transformations (‘tailored’ biomass, generated in Thrust 3). We will develop catalysts for selective hydrogenation of lignin, investigate bio-inspired selective oxidative dealkylation of lignin that targets specifically the benzylic group, and establish tandem catalytic reactions for deoxygenation of polyalcohols, derived from cellulose, followed by C-C bond formation to afford branched alkanes. Second, with the same range of biomass materials, we will study thermal processes in the presence of catalysts. A knowledge gap exists for detailed understanding of how fast-hydropyrolysis and *in situ* hydrodeoxygenation in the presence of appropriate catalyst(s) can lead to increased liquid fuel yields. In both routes, our focus is molecular understanding of catalyst-biomass interactions and determining the physical descriptors that control reactivity and selectivity. Development of advanced mass spectrometric tools will enable rapid molecular-level characterization of complex mixtures of reaction products. Underpinning the experimental approaches will be a tightly-integrated computational approach that models interactions of potential catalysts with biomass structure for a more rational selection and design of catalysts.

Thrust 2. Achieve an atomic-to-macromolecular scale understanding of the interactions of catalysts with the chemical and physical structures of lignocellulosic biomass. To provide critical knowledge of how biomass interacts with catalysts, we will use structural biosensors with intrinsic or engineered carbohydrate- and protein-binding specificity, sophisticated imaging technologies and advanced bioanalytical tools to define the chemical structure and physical properties of biomass, its components and genetic variants, during catalytic transformations. We will develop models and cyberinfrastructure for integrated data visualization from Ångström to micron scales, including computational models of cell wall assemblies in various interaction configurations with metallo- and other chemical catalysts. DOE-BES user facilities at Argonne National Laboratory and the Oak Ridge National Laboratory will be utilized for advanced scattering and imaging techniques.

Thrust 3. Engineer tailored biomass for highly efficient, direct catalytic conversion to liquid fuels and value-added products. A key aspect of catalyst-substrate interactions is the accessibility of catalysts to the chemical bonds with which they are designed to react. The tools of plant molecular biology and genetics have enabled a revolution in our ability to produce plants with modified characteristics. We have strategies to deliver metal catalysts throughout the cell wall structure and to create functionalized sites poised for catalytic transformations. We will engineer biomass variants to incorporate catalysts, co-catalysts, or functionalized catalytic sites into cell walls as the plant grows, simplifying reaction steps in future catalytic bioprocessing. Our ability to incorporate plant-generated *Trojan horse* catalysts or catalyst scaffolds depends upon a deep understanding of cell wall assembly mechanisms and the chemical structure and physical properties of the biomass.

The new fundamental knowledge gained will form the basis for the next generation catalysts and reaction chemistry for conversion of biomass to liquid fuels and chemical feedstock. The long-range impact of success in our research mission will be to more than double the carbon captured into fuel from biomass over biological conversion routes, and expand the product range beyond ethanol to alkanes and new energy-rich aromatic liquid fuels and other value-added products that retain the current liquid fuel infrastructure.

Center for direct Catalytic Conversion of Biomass to Biofuels (C3Bio)	
Purdue University	**M. McCann (Director)**, M. Abu-Omar (Associate Director), R. Agrawal, N. Carpita, C. Chapple, K. Clase, N. Delgass, H. Kenttamaa, N. Mosier, F. Ribeiro, G. Simpson, C. Staiger, D. Szymanski, K. Thomson
National Renewable Energy Laboratory	M. Himmel, S-Y. Ding, M. Tucker, M. Crowley, B. Donohoe
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Contact: Maureen C McCann
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Energy Frontier Research Center for Solid-State Lighting Science
EFRC Director: Jerry A. Simmons
Lead Institution: Sandia National Laboratories

Mission Statement: Exploring energy conversion in tailored photonic structures and materials to enable revolutionary new phenomena relevant to light emission and other energy technologies.

The overarching theme of our EFRC is the *exploration of energy conversion in tailored photonic structures*, a theme that is at the heart of solid-state lighting and other energy technologies, and a theme of major scientific interest as discovery-class research in its own right. We have organized this EFRC into three scientific Thrusts. Within each Thrust are a number of project tasks, which we refer to as “Challenges.”

Our first scientific Thrust is **“Beyond 2D: Luminescent Nanowires, Nanodots and Hybrid Structures.”** In this Thrust, we will study energy conversion routes in 1D and 0D nanostructures that go beyond the conventional 2D planar heterostructures typical of solid-state lighting technology. These nanostructures are scientifically interesting in their own right, as vehicles for the science of the very small, and for studying how energy quantization and conversion are influenced by dimensionality and proximity to surfaces and interfaces. Also, because of fundamental differences in how lower dimensional structures are synthesized and how they accommodate lattice mismatch and strain, these structures will allow study of defect-mediated energy conversion routes different from those occurring in traditional 2D heterostructures. The first technical Challenge in this Thrust is “Nanowires: Synthesis and Properties of Radial Heterostructures,” in which we will explore the relationship between the synthesis and resulting composition and microstructure of 1D nanowires, with an emphasis on developing the ability to tailor the densities of particular kinds of point and extended defects. The second Challenge is “Nanodots: Nonlinear Luminescence Dynamics,” in which conversion of charged carriers into photons can be extremely efficient, but is also strongly influenced by particle size, microstructure, surface functionalization, and chemical environment.

Our second scientific Thrust is **“Beyond Perturbations: Light and Matter in Subwavelength Photonic Structures.”** In this Thrust, we will study energy conversion routes in subwavelength photonic structures in which electromagnetic fields are stronger or more localized, and photonic densities of states more exquisitely controlled, than in structures typical of current solid-state-lighting technology. Such extreme conditions are scientifically interesting in their own right, as vehicles for the science of coherent, many-body phenomena. And, as new energy conversion routes are explored, entirely new solid-state-lighting materials structures may arise from their understanding. The first Challenge area is “Strongly Coupled Exciton-Photon Systems,” in which we will explore strong coupling between excitons and photons in optical microcavities containing active wide-bandgap GaN-based materials. The second Challenge is “Surface Plasmonic

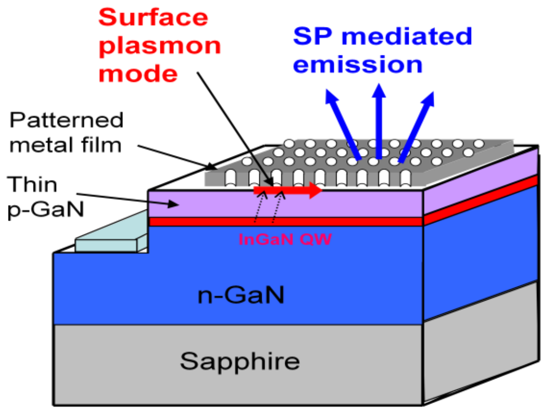

Figure 1. InGaN plasmonic LED structure.

Intermediaries to Exciton-Photon Interactions," in which we will explore the possibility that surface plasmons, with their strong confinement and greatly enhanced local electromagnetic fields, might someday be useful as intermediaries in the energy conversion process from excitons to free-space photons.

Our third scientific Thrust is: **"Wide-Bandgap Materials and Properties: Foundational Understanding and Beyond."** In this Thrust, we will develop a deeper understanding of the synthesis of wide-bandgap materials, and the complex interplay between their defect and luminescent properties – both as applied to current solid-state lighting as well as to the first two "beyond" scientific Thrusts. The first Challenge within this Thrust is "Point Defects in InGaN: Microscopic Origin and Influence on Macroscopic Luminescence," in which we aim to understand the relationship between specific material defects, their dependence on various synthesis conditions, and the production or lack of specific kinds of InGaN luminescence. The second Challenge is "Competing Energy Conversion Routes in Light-Emitting InGaN," where we seek to understand radiative efficiency, which is due to the competition between radiative pathways and undesirable non-radiative pathways that produce heat instead of light. For InGaN materials, there is a complex array of potential non-radiative processes that presently limit the radiative efficiency but are quite poorly understood.

Throughout this EFRC, our emphasis will be on fundamental science enabled by integrated, interdisciplinary capabilities: linking nano-materials design, synthesis and characterization; linking theory and experiment; and linking scientific understanding of isolated phenomena in model systems with empirical observations on relevant technology platforms. Advances in nano-fabrication and nano-characterization will enable such explorations in unusual nanostructure compositions and instantiations, and under experimental conditions specifically tailored to expose particular energy conversion processes. Building on our strengths in tool creation and allied technologies, we will also place an emphasis on research tools (synthesis, characterization, and modeling) that both draw upon science and can be used to enable scientific investigations.

Energy Frontier Research Center for Solid-State Lighting Science (SSLS)	
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Rensselaer Polytechnic Institute	E. F. Schubert
University of New Mexico	S. R. J. Brueck
Northwestern University	L. J. Lauhon
University of Massachusetts Lowell	D. Wasserman
Los Alamos National Laboratory	V. Klimov, R. Prasankumar
Philips Lumileds Lighting	M. R. Krames
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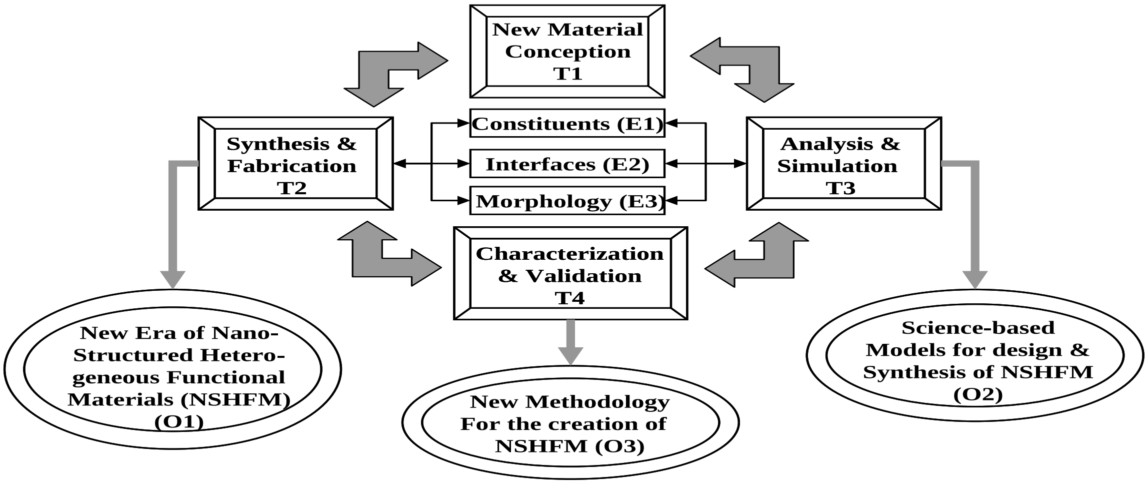
Heterogeneous Functional Materials Center (HeteroFoaM)
EFRC Director: Kenneth Reifsnider
Lead Institution: University of South Carolina

Mission Statement: **It is the mission of this EFRC to establish foundations of understanding and control science that enable the prescriptive design and ordered synthesis of the local compositions, interfaces, and morphology of heterogeneous material systems for specific functional behavior and system performance.**

Material systems consist of multiple materials combined at multiple scales (from nano- to macro that actively interact during their functional history in a manner that controls their collective performance as a system at the global level. Examples include composite mixed-conductors, nano- or micro-structured heterogeneous materials, mechanical alloys, nano-structured interfaces and heterostructures, and many other combinations that typically serve as the heart of engineering devices such as fuel cells, electrolyzers, electrodes, photovoltaics, combustion devices, fuel processing devices, and functional membranes and coatings. The functional behavior of these materials occurs at multiple scales of time and length.

For heterogeneous functional materials (left), the nano-morphology is a critical element of the material conception and design, and the material is not defined until the synthesis is defined. A diagram of our approach appears in the schematic below. The left hand side of the chart focuses on how to make the materials (including modeling of synthesis and processing) and the right hand side of the approach chart focuses on how the heterogeneous functional systems work, based on how they are made. The backbone of our philosophy is finding science relationships between how these special heterogeneous materials are made and how they work (the center of the chart). Creation of the science bridge needed to do that will be the responsibility of our teams of experts, which have been focused in three areas, constituent properties and functional behavior (E1), interface properties and functional behavior (E2), and morphology of the phases (including size, shape, connectivity, scales, etc., E3).



Outputs of the approach will be nearly continuous, and in three major categories, as shown in the figure (O1-O3). From the left hand side of the chart, new material systems and synthesis and processing methods that work will be made available to the outside community of engineering and device designers (O1). On the right, models and simulations will be developed and made available to others so that the science done by the group can be quickly extended to other requirements (O2). And, equally important, from the characterization and validation work (T4), methodologies for evaluating these materials (a special challenge) and for validating models (equally challenging) will be provided to the community (O3).

Several elements of this strategy provide critical benefits and advantages. First, synthesis and modeling play critical, equally important roles since heterogeneous materials are not defined until the process that makes them is defined. ***It can be said that the primary goal of this research program is to build a science bridge between how we make Nano-structured Heterogeneous Functional Materials (NSHFM) and how they work as described by multi-scale models.*** But only the foundations of that bridge are present. We must build from both ends. We must use the breakthroughs in computer-driven additive (and other) synthesis methods to make the best materials we can conceive of and use the best models we can develop to construct a foundation for understanding those materials and to inspire and support the advancement of creative concepts. The Center structure of this program is essential to make this happen. Second, the present approach fully embraces the role of geometry at the nano-level. We will require that field equations be developed for all aspects of the representations of functional behavior, so that computer-driven representations of multi-physics behavior at the local level can be used to design the nano-structure, specifically and precisely, as well as to eventually drive the synthesis processes. This is a major departure from homogeneous domain and chemical rate models that do not capture this critical element of heterogeneous materials. The present approach recognizes that advances in synthesis and fabrication have brought us to the threshold of controlling local morphology, as a function of field variations in the independent variables (temperature, concentrations, etc.) that are the inevitable reality of any and all real devices, especially if they are large enough to be of use to our society.

Heterogeneous Functional Materials Center (HeteroFoaM)	
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Rochester Institute of Technology	D. Cormier
Princeton University	E. Carter, M. Haataja
University of California Santa Barbara	R. McMeeking
University of Connecticut	W. Chiu
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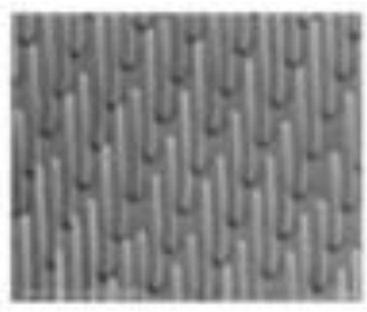
Center for Energy Nanoscience
EFRC Director: P. Daniel Dapkus
EFRC Lead Institution: University of Southern California

Mission Statement: Our EFRC will create new technologies for solar cells and LEDs based on nanostructured semiconductors, organic semiconductors, and hybrid structures to lower the cost and increase the efficiency of existing technologies.

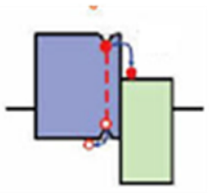
The EFRC program to study emerging materials in solar energy and solid state lighting has as its goals the invention of new solar cell and LED designs based on nanostructured and organic materials. This program is motivated by the following vision: **to demonstrate new technologies based on novel nanostructure and organic materials that will enable photovoltaic energy conversion to become a significant portion of the world's electricity infrastructure and solid state lighting to become a dominant lighting technology in the world**. To accomplish these goals, we have assembled an expert interdisciplinary team from four major research universities. This team has expertise in nanostructure synthesis, organic molecule and polymer design and synthesis, optical and transport characterization of nanostructures, petascale simulations of materials structural, optical and transport properties and device physics, fabrication and characterization. This team will undertake fundamental studies in these areas to develop a broad understanding of the relationship between materials structure and composition and the ultimate device performance. From this understanding we expect new device designs will emerge that capitalize on our ability to engineer the materials at the molecular and atomic level in these systems. We envision both nanostructured semiconductors and organic materials being synthesized by low energy processes, allowing the the resultant device concepts to be assembled on low cost media, leading to cost effective implementation. Although the development of these cost effective processes is not part of the activities of the center, our researchers will be mindful of the eventual cost goals of the applications in their choices of materials and processes. We expect that the outcome of our research will be the rational identification and demonstration of designs for solar cells and LEDs that exhibit the performance goals we have identified as our targets.


Inorganic Semiconductor
Nanorod Array

The objectives of our research during the first five years will be to develop the fundamental control at the atomic/molecular scale, the understanding of materials properties and processes at that level to permit the rational design of solar cells and LEDs based on these novel materials, the understanding of interface and structural characteristics that control device performance, and the path to the fabrication of devices that demonstrate performance comparable to or exceeding current technology.

Small Molecule Organic
Semiconductors

Our research plan capitalizes on the synergy that exists between emerging technologies for solar energy conversion and solid state lighting by conducting a program of research involving leaders in organic materials and devices and semiconductor nanostructure materials and devices to exploit the opportunities that we believe will accrue by applying these new materials structures in both application areas. We have identified materials technologies with the greatest long term potential to dramatically improve the performance and reduce the cost of solar cells and light emitters. Many of the technical and economic challenges that exist in both areas can be addressed by adopting the philosophy underlying our program. The major challenge to the economics of these technologies can be addressed by employing **high performance components** that can be fabricated in **thin structure designs on low cost substrates**. For this reason we have chosen to focus our efforts on **nanostructured semiconductor materials, organic materials and hybrid structures between them.** Organic materials can be deposited in nanometer thick films by solution or low temperature vacuum deposition methods, on glass and plastic substrates to produce photovoltaic devices and light emitting diodes. Similarly, nanostructured semiconductors can be synthesized at low temperatures on low cost materials in structures whose properties approach those of single crystal thin layers and whose characteristics can be **manipulated at the atomic level**. Given these properties, we believe that there is also an opportunity to explore hybrid structures between the materials that combine the best of both materials and may allow us to produce structures that exceed the performance of components using either one alone.



Organic Heterostructure Solar Cell Schematic

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University of Southern California	P.D. Dapkus (Director), M. E. Thompson, S. E. Bradforth, R. L. Brutchey, S. B. Cronin, R.K. Kalia, J. G. Lu, A. Nakano, J. D. O'Brien, G. Ragusa, B. C. Thompson, P. Vashishta, C. Zhou
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Center on Nanostructuring for Efficient Energy Conversion (CNEEC)
EFRC Director: Stacey Bent and Fritz Prinz
Lead Institution: Stanford University

Mission Statement: CNEEC seeks to understand and solve cross-cutting fundamental problems at the nanoscale for improved energy conversion efficiency in devices such as photovoltaics, fuel cells, and batteries.

The overarching goal of the Center is to increase the efficiency of energy conversion devices by manipulating materials at the nanometer scale. We will develop the fabrication and characterization methodologies to understand how nanostructuring can optimize transport, light absorption, and reaction kinetics and thermodynamics in materials, each of which will be used to improve performance and efficiency in energy conversion and storage devices. Our research will provide a scientific foundation of underlying physical and chemical phenomena shared by a diverse range of energy conversion processes, and exploit them in devices for break-out high-efficiency, cost-effective energy technologies.

CNEEC will support three research thrusts:

- Tuning Thermodynamics/Kinetics by Nanostructuring (TRG1)
- Photon Management (TRG2)
- Optimizing Charge Transport at Reduced Sizes and Dimensions (TRG3)

We view these three themes as universal cross-cutting topics which underlie virtually all attempts to improve energy conversion efficiency. Figure 1 symbolizes our center concept. We will employ nanostructuring to generate high gradients, high surface-to-volume ratios, and low dimensionality, and identify ways in which such engineered structures can enhance materials properties such as light absorption, charge transport, and catalytic activity that are critically important for many energy conversion systems. We will exploit these properties to tune thermodynamic equilibria and kinetic properties, to vary photonic behavior through quantum confinement for efficient photon capture, and to reduce distances for charge transport. We will manipulate sub-nanometer particles – namely electrons, photons, ions, atoms, and molecules – by tuning material properties through nanostructuring.

Based on such fundamental work, we will build and test device structures that demonstrate how our fundamental advances can improve the efficiency of photovoltaics, batteries, photoelectrochemical fuel synthesis, fuel cells, supercapacitors, and hydrogen storage. The nanoscale design principles we will pursue will provide the foundation for a sustainable energy future that will require a collection of energy technologies working in concert to produce, store, and consume the 20 TW of energy that humans will soon demand. Although there are many existing technologies for energy conversion, they cannot provide renewable or sustainable solutions at scale because they are either too inefficient or too expensive. It is thus critical to improve the efficiency of these conversion devices and systems.

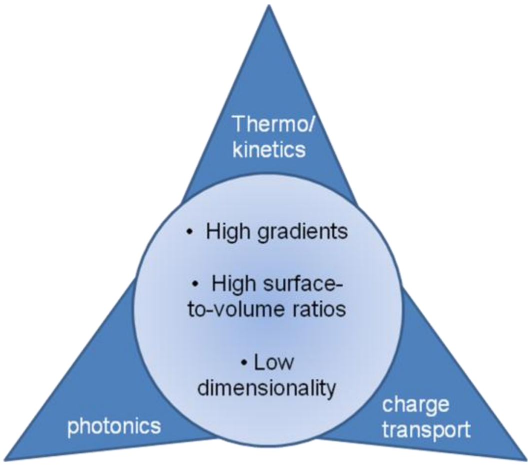

Figure 1. CNEEC concept and approach for improving energy efficiency.

The knowledge gaps that CNEEC research programs aim to address are as follows:

Thermodynamics / Kinetics (TRG1&3): Conversion efficiency is highest near thermodynamic equilibrium. Virtually any deviation from equilibrium results in irreversible energy losses. Energy conversion at high rates requires large overvoltages, which in turn reduce efficiency. We will improve energy efficiency by manipulating the surface-to-volume ratio of characteristic device features, thereby influencing the free energy of surface-bound chemical reactions.

Photonic Absorption (TRG2): By building energy conversion devices with features below a characteristic length scale of typically 10's of nm, we can modify electronic structures such as bandgap and Fermi level. Quantum confinement structures, in which the size influences the electronic properties, allow us to tune the interaction of light and electrons. They also enable us to control the probability of electronic transition from a substrate to an adsorbate. Quantum confinement allows us to control properties such as light absorption and catalysis, which are important for photovoltaic (PV) and photoelectrochemical (PEC) devices.

Charge Transport (TRG2&3): To improve the efficiency of next generation energy conversion and storage devices, we must learn to control charge transport phenomena in the range of a few nanometers to hundreds of nanometers. Thermodynamic losses accompany any material transport. The rate of loss depends on the finite rates of diffusion and interfacial reactions involving ionic species and scattering, charge recombination, and the probability of trapping for the electronic species. We can ameliorate the adverse effects of these events by reducing the charge transport length.

These three properties – thermodynamics/kinetics, photonics, and transport – form a coherent thread through virtually any energy conversion scheme. We must understand and control these properties to create next-generation energy utilization, storage, and conversion devices. The Center will remove key barriers to realizing such devices by improving fabrication methods, modeling methods, and characterization tools.

The Stanford team brings expertise in *ab initio* design, synthesis, characterization, simulation, and device fabrication. Our partners will complement the program in both experimental and theoretical efforts. The Technical University of Denmark brings world-class expertise in theory to elucidate underlying phenomena and to guide the design of new materials and structures. Carnegie Institution offers expertise in biological sciences and bioengineering. HRL Laboratories provides first-rate scientific research and a link to industrial partners.

Center on Nanostructuring for Efficient Energy Conversion (CNEEC)	
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Carnegie Institution	A.R. Grossman
Danish Technical University	J.K. Nørskov
HRL Laboratories	P. Liu, J.J. Vajo

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Northeastern Center for Chemical Energy Storage (NECCES)
EFRC Director: Clare P. Grey
Lead Institution: Stony Brook University

Mission Statement: To identify the key atomic-scale processes which govern electrode function in rechargeable batteries, over a wide range of time and length scales, via the development and use of novel characterization and theoretical tools, and to use this information to identify and design new battery systems.

The design of the next generation of lithium-ion batteries (LIBs) requires both the development of new chemistries and significant improvements in our fundamental understanding of the physical and chemical processes that occur in these systems. The mechanisms by which LIBs operate are often extremely complex and interconnected, occurring over timescales that vary from femto-seconds to years, and over equally broad spatial scales. Progress in this area requires a multidisciplinary approach involving both experiment and theory, making use of existing methodologies, while developing new tools specifically designed to investigate electrode processes in real time. The specific goals of this center are to I. develop a fundamental understanding of how electrode reactions occur, and how they can be tailored by appropriate electrode design (doping, particle size, shape, composite structure), to (i) identify critical structural and physical properties that are vital to improving battery performance, and (ii) use this information to design new battery systems. Examples of electrode materials chosen for investigation include doped olivines, layered materials and conversion chemistries based on the FeF_3-FeOF system. II. Develop new diagnostic methodologies of relevance to the entire battery community. An emphasis will be placed on the development of *in situ* methods that use multiple experimental tools simultaneously or that combine imaging with spectroscopy. The new materials synthesis program will be guided by theoretical predictions that result from this effort. To achieve these goals we have established four closely coupled thrusts that will focus on areas of critical relevance to improving energy storage:

Thrust 1: Cross-cutting research: Developing the characterization and diagnostic tools to investigate battery function. The development of novel characterization tools and methodologies with increased spatial, energy and temporal resolution will provide fundamental understanding of electrochemical energy storage systems. Such multi-dimensional analysis will be used to reveal and deconvolute complex and interdependent processes in electrodes, electrolyte and at their interface. Four major developments are proposed: (i) *in situ* NMR studies of battery materials, (ii) *in situ* imaging and spectroscopy of surface and bulk processes in composite electrodes (see for example, Fig. 1) and model single particle nano- and

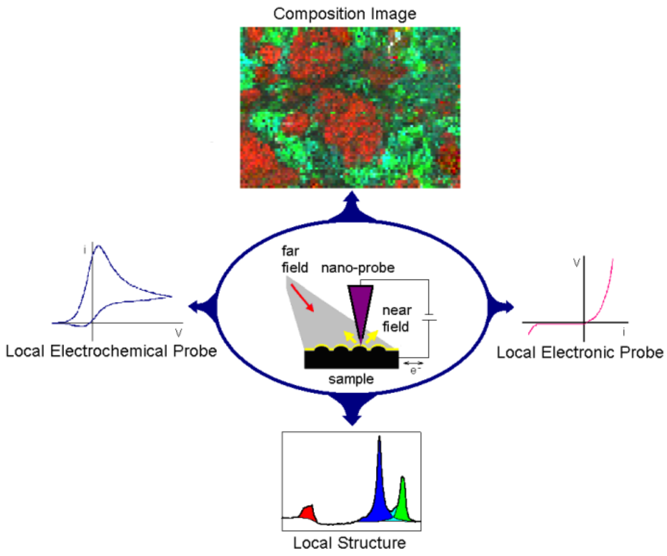

Fig. 1. A multifunctional interfacial probe.

micro-electrodes, and (iii) *in situ* analytical TEM and Electron Energy Loss Spectrometry (EELS) investigations of the chemical, structural, and electronic properties of electrodes at the nanometer scale, and (iv) *in situ* pair distribution function (PDF) analysis of local and intermediate range structure in functional nano-crystalline or disordered materials. We will make use of BES synchrotron facilities available at Brookhaven National Laboratory and Argonne National Laboratory (e.g., for *in* and *ex-situ* PDF, X-ray diffraction and X-ray absorption spectroscopy), and the Molecular Foundry at Lawrence Berkeley Laboratory and the Center for Functional Nanomaterials (e.g., for TEM and nanofabrication).

Thrust 2. Cross-cutting research: Theory and computational modeling to understand and predict kinetic phenomena in electrode materials. Computational modeling will be used to accelerate the discovery of battery materials with higher power and energy density, and their integration in practical battery systems, by creating an understanding of the processes by which they store Li. Modeling at scales from the electronic and atomistic through the mesoscopic scale will be used.

Thrust 3: Intercalation chemistry. Experimental studies combined with computational modeling will be used to understand the fundamental limitations of structure-retention reactions, of both single phase and multi-phase type. This will allow the discovery of the next generation battery materials that have significantly higher energy densities, yet maintain today's highest reaction rates, and maintain or self-heal their structures over thousands of redox cycles.

Thrust 4. Conversion chemistries. Conversion chemistries offer a potential path to high energy density electrodes and also new ways to form materials on a very fine nm scale. As opposed to most present day intercalation systems which operate through a single or at most two phase process, conversion materials operate at the minimum of a three phase process, sometimes four. All of these phases are in a dynamic state and electrochemically formed and reformed on a scale of 1-10nm. The goal will of this thrust will be to establish an understanding of the phase development, redox, the ionic and electronic transport involved at such scales which allow these systems to operate and to identify kinetically limiting processes.

Northeastern Center for Chemical Energy Storage (NECCES)	
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Binghamton University	M.S. Whittingham (Assoc. Director, Thrust 3 leader)
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Understanding Charge Separation and Transfer at Interfaces in Energy Materials (EFRC:CST)

EFRC Director: Paul F. Barbara

Lead Institution: University of Texas at Austin

Mission Statement: The EFRC:CST aims to elucidate the critical interfacial charge separation and charge transfer processes that underpin the function of highly promising molecular materials for organic photovoltaic (OPV) and electrical-energy-storage (EES) energy applications.

This EFRC will effectively address a major scientific roadblock to achieving U.S. energy security: the limitations in the basic scientific understanding of interfacial charge separation and transfer processes of nanostructured OPV and EES materials for energy needs. The mechanistic understanding of interfacial charge separation and transfer processes in nanomaterials is in its infancy, without a broadly accepted theoretical description. Moreover, existing experimental tools and theoretical models are insufficient to definitively address the many outstanding scientific issues for the complex nanomaterials in this field. Instead, completely new multidisciplinary approaches, featuring greater molecular-level precision and accuracy and closer coupling between theory and modeling, are necessary to drive the fundamental aspects of this field forward. Therefore, we have constructed a research program that is uniquely well-suited to critically advance the fundamental understanding of charge separation and transfer processes through a highly coordinated and focused scientific approach that features closely coupled theoretical and experimental components. Our approach is based on two critical strategies:

The EFRC:CST will support a set of coordinated research projects that study unique and novel interfacial prototypes that climb the ladder of molecular complexity from well-defined epitaxial crystal/crystal interfaces, through isolated crystal/crystal interfaces, to model polymer/crystal interfaces and then to actual OPV and EES devices.

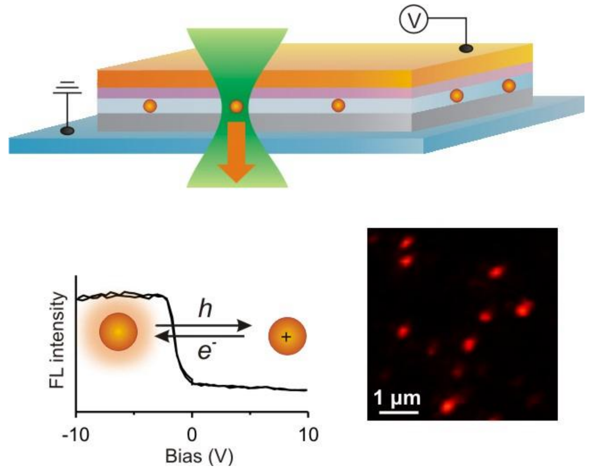
The EFRC:CST will use powerful, state-of-the-art imaging and sub-ensemble methods (e.g., single particle spectroscopy and imaging) to make correlated measurements of structure and charge separation/transfer processes on the molecular scale for each type of interfacial prototype.

Together these two strategies serve as a foundation to obtain experimental data that will be modeled and analyzed by advanced theoretical and computational methods, leading to new insights on the molecular-level mechanisms of charge separation and transfer functions of complex OPV and EES nanostructured materials.

Our program is designed to address three distinct areas (thrusts) where enhanced fundamental understanding of charge separation and transfer in nanomaterials is critical for energy needs. **Thrust I, Interfacial Charge Separation,** aims to obtain new molecular-level information on the yields of exciton charge separation in the OPV mechanism of actively investigated OPV donor/acceptor material combinations (e.g., oligothiophene/C60). To achieve this goal we will use coupled theoretical and experimental methods, including sub-ensemble techniques (e.g., two-photon photoemission spectroscopy) to study powerful interfacial prototypes (single crystals, thin films, nanostructured arrays) of OPV materials. Such studies will allow us to obtain major breakthroughs in the molecularly precise and accurate understanding of how and why the "prompt" quantum efficiency of interfacial charge separation of excitons depends on donor and acceptor molecular structure, orientation, and packing; the molecular organization at the interface; the driving force for charge separation; disorder of the materials; exciton effects; and other related factors.

Thrust II, Interfacial Charge Transfer, will couple single-molecule spectroscopies, chemical imaging, electrical measurements, and molecular-level theoretical modeling to obtain new insights on the charge transfer and recombination processes of OPV nanostructured materials (single-nanoparticle interfaces, planar nanostructures). An example of a fluorescence voltage–single-molecule-spectroscopy (FV-SMS) study to be carried out in Thrust II is shown here. Through such studies we will develop a molecularly precise understanding of factors that control interfacial charge transfer rates across donor/donor, donor/acceptor, and acceptor/acceptor interfaces, as well as investigate the trapped charges in OPV materials and their effects on altering OPV device efficiencies.

For **Thrust III, Li$^+$-Coupled Charge Transfer,** we will conduct highly coordinated experimental and theoretical investigations of model solid-liquid interfaces in various interfacial prototypes (Si and Ge nanorods; nanospheres and patterned arrays; phospho-olivines; layered oxides) to understand fundamental lithium-ion-coupled electron transfer reactions at interfaces in EES materials. In particular, we will explore the interdependency of particle size, composition, and structure in an effort to understand two-phase versus single-phase Li$^+$ storage phenomena in nanoscale lithium storage materials. We will also elucidate factors that govern charge transfer reactivity in model lithium alloy nanostructures by exploring the influence of size, morphology, and electrode configuration on Li$^+$-coupled charge transfer, volume expansion/contraction processes, and alloy phase formation mechanisms.



FV-SMS setup and sample charge/discharge data for a hole-injection device consisting of insulating (grey), hole transporting (purple) and nanoparticle layers. Data obtained from such experiments allows for the probing of charge transfer rates in single polymer molecules.

While the underlying materials issues raised in the three thrusts are distinct, the experimental and theoretical methods developed in the thrusts are highly analogous and synergistic. In fact, several PIs have projects in more than one thrust. Each of these thrusts will be addressed through several ongoing research projects as well as seed projects.

If successful, this EFRC will produce three important outcomes: (1) new OPV and EES materials that are rationally designed to be substantially more efficient than current state-of-the-art materials; (2) a new suite of molecular-level tools to be used both in academia and in industry to evaluate and optimize these new molecular materials; and (3) the education of a new generation of energy researchers who are trained to produce these materials and utilize these molecular tools.

Understanding Charge Separation and Transfer at Interfaces in Energy Materials (EFRC:CST)	
University of Texas at Austin	**Paul F. Barbara (Director)**, A. J. Bard, C. Bielawski, J. Chelikowsky, A. Dodabalapur, P. Ferreira, V. Ganesan, J. Goodenough, G. Henkelman, B. J. Holliday, B. A. Korgel, A. Manthiram, P. Rossky, K. J. Stevenson, D. A. Vanden Bout, L. J. Webb, K. A. Willets, X. Zhu
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Center for Frontiers of Subsurface Energy Security

Gary A. Pope
The University of Texas at Austin

Mission Statement:

Currently humans extract most of the fuel for the global economy from underground. The byproducts of consuming this fuel enter the atmosphere or remain on the surface. This situation is no longer tenable. A critical step toward future energy systems will be the ability to cycle fuel byproducts back to their original home: the Earth's subsurface. Applications of this concept include storing CO_2 in deep geologic formations and securing radioactive materials in appropriately engineered repositories. Our goal is to fill gaps in the knowledge base so that subsurface storage schemes are reliable *from the moment they open*.

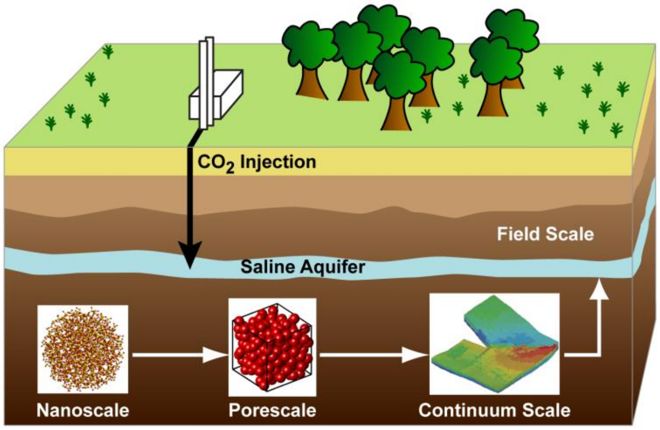
Project Description:

Recent theoretical and experimental advances have opened previously inaccessible avenues for understanding material properties at scales less than 100 nanometers. The same advances also present opportunities to control material behavior in novel ways. The central theme of this proposal is **harnessing these advances to explain reactive transport in geologic systems**.

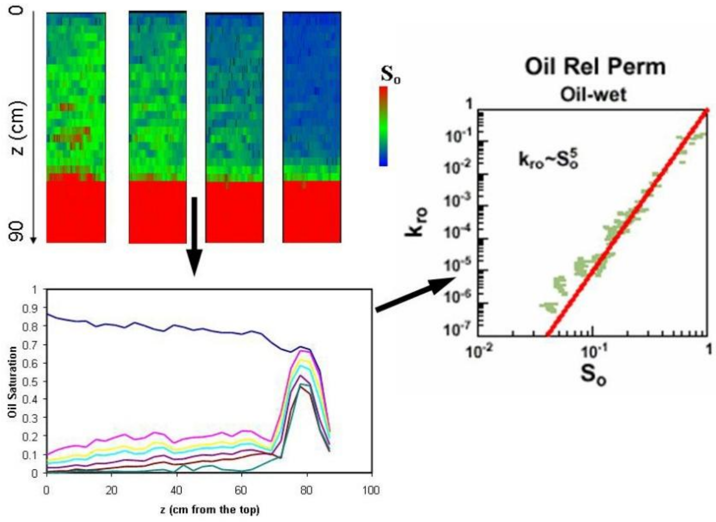
The movement and reaction of species in multiple fluid phases through voids in rocks has been studied for decades. Yet our ability to predict large-scale, long-term behavior is not impressive. Nearly every forecast over human scales (decades) requires substantial revision over time. Too often the reason is that our conceptual and mathematical models leave out or misrepresent features that turn out to be crucial. The current knowledge base is therefore inadequate for one of the greatest challenges for 21st century energy systems: the secure sequestration in the Earth’s subsurface of byproducts from fuel consumption.

Two scientific Grand Challenges contribute to the gap between forecast and outcome in geologic systems. First, byproduct storage schemes will operate in a **far-from-equilibrium state.** Complicated behavior, including self-reinforcing and self-limiting transport, emerges during such processes. Central to the complexity is the coupling between biogeochemical alteration, transport properties, and mechanical loading. Much of this coupling can be traced to phenomena at very fine scales: the cell wall of a microorganism living in a pore, or molecules at a fluid/mineral interface. Consequently we expect that new materials, new methods for characterization at sub-pore scales, and new modeling concepts and tools will enable an urgently needed advance in our understanding of subsurface flow and transport.

The second Grand Challenge is to explain the **emergence of patterns** and other manifestations of correlated phenomena. Emergent behavior can arise at several length scales even from a single set of processes, so recognizing this behavior is not always easy. Solutions to the unresolved challenge of discerning the causes of emergent behavior and capturing them in a model will have profound implications on 21st century energy systems. For example, the unforeseen emergence of preferential flow paths can defeat an otherwise secure repository. Tailoring the interaction at a fluid/mineral/microbe interface, on the other hand, could render a system self-sealing. To address those two Grand Challenges, CFSES is organized around four focus areas. The first focus area will investigate natural subsurface processes and engineered systems in far-from-equilibrium states at very small scales (molecules to pores). The second focus area will characterize patterns and behaviors of multiphase reactive flow and mechanics that emerge between the pore and the continuum scales. The third focus area will analyze and characterize the coupled mechanics, reactions, flow, and transport that have their sources at the pore and continuum scales and reveal themselves between the continuum and field scales. Finally, the fourth focus area will develop multiphysics, multiscale modeling and simulation schemes that incorporate the findings of the other three tasks.



Geological storage of greenhouse gases from pore to continuum scales.



Mesoscale CT data versus time can yield residual saturations and relative permeability, revealing behavior not accessible in traditional experiments.

Center for Frontiers of Subsurface Energy Security (CFSES)	
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Center for Catalytic Hydrocarbon Functionalization
EFRC Director: T. Brent Gunnoe
Lead Institution: University of Virginia

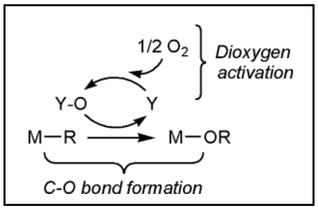
Mission Statement: The CCHF fosters collaborations between groups with expertise in catalysis, electrochemistry, bioinorganic chemistry, materials chemistry and quantum mechanics to enable fundamental advancements in the design and development of next generation catalysts for selective, low temperature, hydrocarbon functionalization.

Catalysts are central to the efficient and clean utilization of energy resources, and they impact all aspects of the energy sector. Catalysts a) mediate the transformation of hydrocarbon raw materials into forms that are useful to the materials, chemistry, power and transportation industries, b) reduce energy consumption and waste production for large scale commodity processes, and c) convert harmful by-products (*e.g.*, by-products of combustion) into more environmentally benign forms. Consequently, catalysis is a cornerstone of the chemical industry; however, maintaining a steady and clean supply of energy to the developing global population and accessing new energy resources will require dramatic advancements in the catalysis arena. A central tenet of the Center for Catalytic Hydrocarbon Functionalization (CCHF) is that the development of advanced catalysts that allow controlled and selective conversion of C-H bonds to C-O and C-C bonds are key to more efficient use of fossil resources as well as future use of solar energy and biomass.

Fossil raw materials, which provide almost all of our energy, are primarily hydrocarbons (molecules that contain only carbon and hydrogen). Unfortunately, the current high temperature processes that convert these raw materials lead to low efficiency, high costs, excessive emissions (including carbon dioxide) and a disproportionate dependence on imported petroleum. In the near term, the increased worldwide demand for energy will be impossible to sustain without dramatic developments that lead to new technologies that optimize the utilization of fossil resources. For example, increasing the rate and selectivity for the transformation of C-H bonds in reactions with oxygen is central to new catalysts that substantially enhance energy efficiency, reduce emissions, increase use of *domestic* resources (*e.g.*, methane from natural gas), and convert carbon dioxide into more environmentally benign forms. The CCHF brings together a broad based collaborative team with the expertise to accelerate advances in fundamental aspects of catalyst technologies required for selective hydrocarbon functionalization. These efforts can have broad impact vis-à-vis increasing domestic energy sources, mitigating negative impact on the environment and providing tools for utilization of biomass and solar energy.

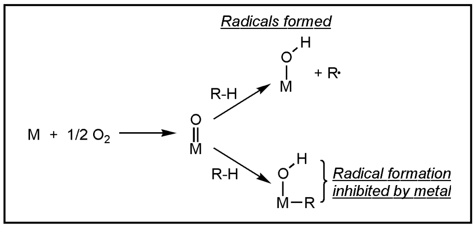
The development of efficient catalysts for the conversion of hydrocarbons into higher value materials (*e.g.*, the conversion of methane to liquid fuels such as methanol) requires novel systems based *on new chemical transformations*. In order to transform hydrocarbons, the catalysts must: a) break at least one C-H bond, b) mediate the formation of a new bond of carbon with a heteroatom {*e.g.*, alcohol production (R-H → R-OH) requires a new carbon-oxygen bond}, and c) release the functionalized product with protection against additional reaction. In order to provide the new science needed to enable chemists to design such smart catalysts, the CCHF will focus on three initial "thrust" areas:

1. New Methods for Carbon-Heteroatom Bond Formation: A primary focus of the CCHF is the controlled (and potentially reversible) conversion of hydrocarbons to "functionalized' materials (*e.g.*, oxygenated compounds such as alcohols). The formation of carbon-heteroatom bonds, one step in overall hydrocarbon functionalization, is a major chemical challenge. For example, reactivity of metal hydrocarbyl complexes (metals with alkyl or aryl ligands) with oxidants to deliver a new C-O bond has been a vexing challenge for this field, and particularly difficult is finding a method to incorporate dioxygen as the oxygen atom source. On the other hand, enzymatic systems routinely use dioxygen to deliver oxygen atoms to hydrocarbons and related compounds. The PIs in the CCHF will pool insight from



complementary backgrounds, including bioinorganic, organometallic, electrochemistry and computational chemistry, to develop new pathways for these transformations and to garner a new atomic level understanding of how the features of the metal work in concert with the oxidant to promote the reactions. We will focus on the design of new classes of organometallic complexes that react readily with oxygen sources, new methods to activate dioxygen into forms that can deliver oxygen atoms, new technologies that permit controlled and reversible C-O bond formation, and computational methods capable of predicting accurately the best materials on which to focus the experiments.

2. New Classes of Metal Oxo Complexes: Nature functionalizes hydrocarbons using metal-oxo complexes (*i.e.,* systems with M=O bonds) in which the metal is in a high oxidation state (*i.e.*, the metal is electron deficient). The ability of chemists to replicate the reactivity of these enzymes using synthetic models is limited. By combining expertise in bioinorganic chemistry, homogeneous and heterogeneous catalysis, and computational chemistry the CCHF will pursue new strategies to synthesize metal oxo systems that provide more controlled hydrocarbon functionalization chemistry. For example, one pursuit will be the design of systems with new electronic structures that are less amenable toward radical reactivity (odd-electron transformations), which generally decreases selectivity thereby decreasing catalyst efficiency. Designing systems that can activate dioxygen, while avoiding radicals, and selectively functionalize hydrocarbons requires significant advances that can only be achieved by combining computational chemistry, organometallic catalysis and bioinorganic themes.



3. Developing new "environments" for hydrocarbon chemistry: A substantial challenge for selective hydrocarbon functionalization, especially partial oxidation, is developing catalytic systems that can react with inert hydrocarbons but that are inhibited toward reaction with the functionalized products, which are almost always more reactive than the starting hydrocarbon feedstock. Most previous work to solve this problem has focused on homogeneous catalysts, since such systems are usually more amenable to tuning of reactivity toward specific substrate selectivity than heterogeneous catalysts. Groups in the CCHF will initiate new avenues for such reactions by designing advanced materials to control reaction environments. These collaborations between molecular and materials chemists will seek catalysts at the nanoscale that provide new modes of selectivity for reactivity with hydrocarbons while limiting reactivity with functionalized products.

Summary: We have mounted collaborative efforts on three parallel developments most likely to provide the new understanding needed for rationale development of novel materials for controlled hydrocarbon functionalization.

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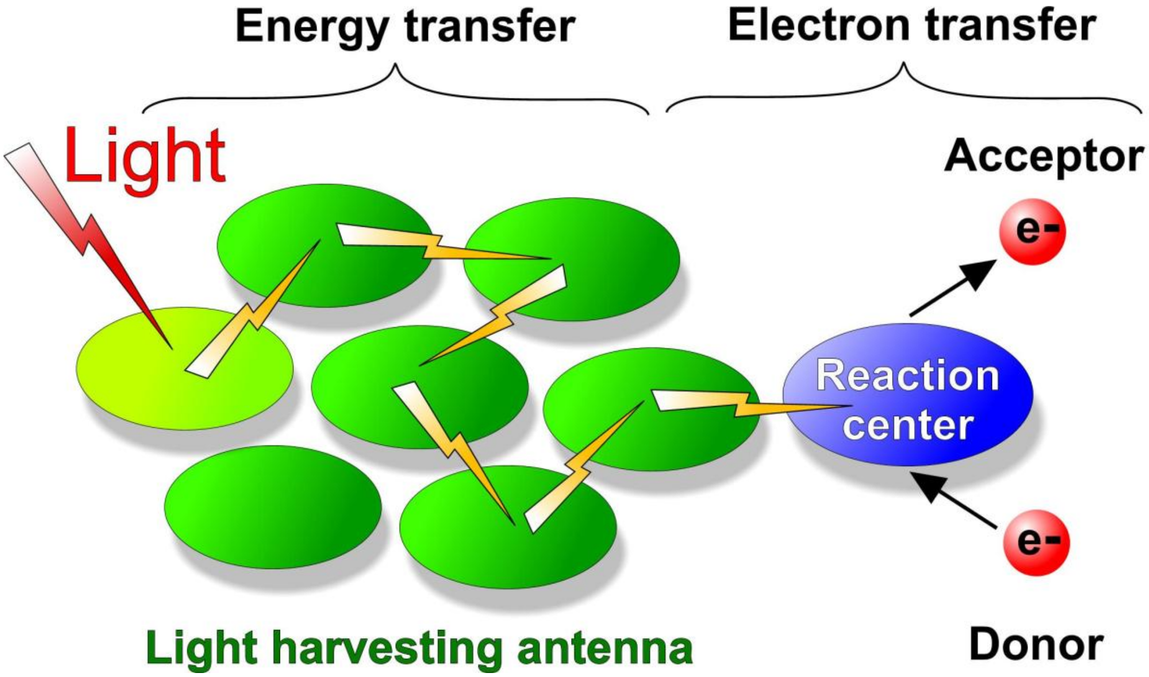
Photosynthetic Antenna Research Center
EFRC Director: Robert E. Blankenship
Lead Institution: Washington University in St. Louis

Mission Statement: The mission of PARC is *to understand the basic scientific principles that underpin the efficient functioning of natural photosynthetic antenna systems as a basis for design of manmade systems to convert sunlight into fuels.*

This Energy Frontier Research Center is a program in basic scientific research aimed at understanding the principles of light harvesting and energy funneling as applied to natural photosynthetic, biohybrid and bioinspired antenna systems. The project will be organized around three programmatic themes:
1 – Natural Antennas: Structure and Efficiency
2 – Biohybrid Antennas: Organization and Implementation
3 – Bioinspired Antennas: Design and Characterization

Specific underlying issues include structure determination of natural antennas using both traditional and novel techniques at different levels of scale as well as the connections between new structural detail and functional characteristics. Other areas of research involve elucidation of how the size and pigment composition of natural antenna systems affect the efficiency of energy conversion as well as how the range of photosynthetically active radiation might be extended into other wavelength regions of the solar spectrum. Additional research goals involve how bioinspired and biohybrid systems can be designed and assembled to use the principles of natural antennas to enhance energy collection and storage.

Methods that will be utilized will include: X-ray crystallography, neutron diffraction and scattering, electron microscopy, photobioreactor growth analysis, scanning probe microscopy, hyperspectral imaging spectroscopy, ultrafast laser fluorescence



spectroscopy, density functional theory, molecular dynamics calculations, surface chemistry, synthetic chemistry, *de novo* protein design, RNAi technology, and recombinant DNA technology.

Significant educational and outreach efforts will be made at the K-12, undergraduate and graduate levels. Advanced electronic communication and networking techniques will be used to keep the team in constant communication, and a yearly “all hands” meeting will bring all the participants together to discuss progress, plans and strengthen collaborations.

Potential outcomes and benefits include elucidation of the basic scientific principles that underlie the efficient functioning of natural photosynthetic antenna systems and how those principles can be translated into biohybrid and bioinspired complexes that will form the basis for next-generation systems for solar energy conversion.

This project will bring together a core of seventeen diverse scientists to form an interdisciplinary team. The team includes five Washington University professors along with five national laboratory participants from Oak Ridge, Sandia and Los Alamos National Laboratories. In addition, six other academic scientists from universities in the US and the United Kingdom and one from a US private research institute round out the team. This international interdisciplinary team brings extraordinary breadth and depth of intellectual and technical expertise to this important research area.

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INVESTIGATOR INDEX

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