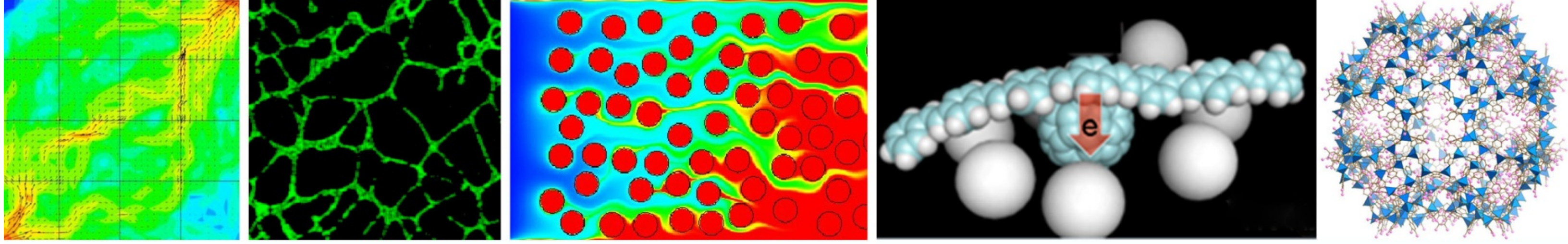


Energy Frontier Research Centers

Technical Summaries

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

January 2011; Revised 07/16/2012
Current version available at http://science.energy.gov/bes/efrc

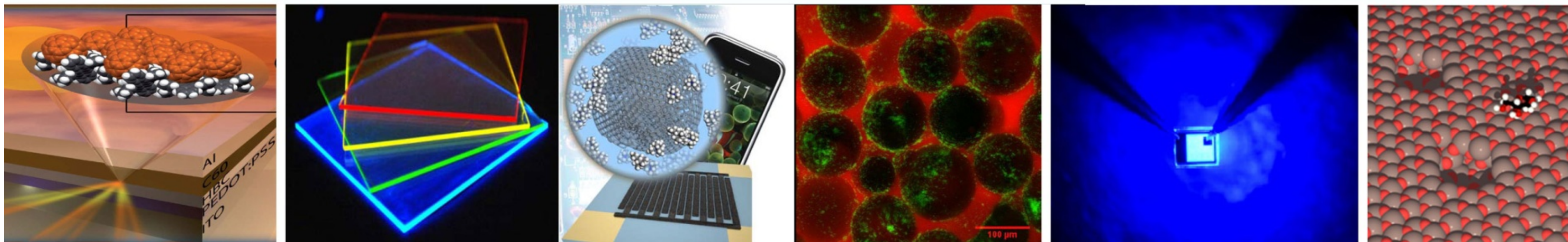
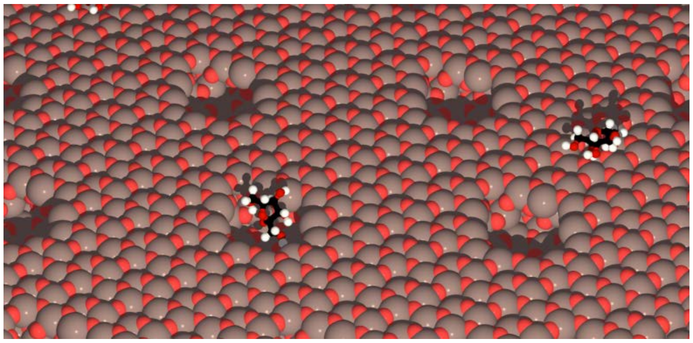


TABLE OF CONTENTS

Institute for Atom-efficient Chemical Transformations (IACT)
EFRC Director: Christopher L. Marshall
Lead Institution: Argonne National Laboratory

Mission Statement: 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 addresses key chemistries associated with clean, efficient utilization of two major 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 are also critical to advancing catalysis science and are major IACT activities. Finally, the ultimate validation of our synthesized, characterized, and computationally modeled catalysts comes from evaluating their catalytic performance, as will feedback for further catalyst design.

IACT may be viewed as consisting of four distinct but intimately interlinked tasks: 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 concentrate on three primary classes of materials:

- **Isolated Mono-Functional Sites**
  This is the conventional picture of heterogeneous catalysts, such as oxide-supported metal particles or an acid/redox site on a bulk oxide surface.
- **Proximate Multi-Functional Sites**
  These are 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 seeks 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 investigate synthesized materials under "real world" conditions, studying the atomic-scale processes that control catalysis. This task provides the insight to develop physically based predictive models of the property of materials synthesized. In situ characterization employs 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 provides theoretical insights at the atomistic level regarding the catalytic properties of new materials and experimental observations. Modeling also provides guidance in the discovery of new catalytic materials.

Catalytic and Chemical Reaction Science

Catalytic and chemical reaction science provides 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 is critical to developing and exploring efficient chemical conversion processes.

Institute for Atom-efficient Chemical Transformations (IACT)	
Argonne National Laboratory	Christopher L. Marshall (Director) , L.A. Curtiss, J.W. Elam, J.P. Greely, J. Jellinek, J.T. Miller, R.E. Winans
Northwestern University	P.C. Stair (Deputy Director), L.J. Broadbelt, M.C. Kung, T.J. Marks, S.-B.T. Nguyen, J.W. Notestein, K.R. Poeppelmeier, E. Weitz
University of Wisconsin – Madison	J.A. Dumesic, T.F. Kuech, M. Mavrikakis
Purdue University	W.N. Delgass, F.H. Ribeiro
Brookhaven National Laboratory	E. Stach

Contact: Christopher L. Marshall, Senior Chemist; marshall@anl.gov; 630-252-4310
http://www.iact.anl.gov

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 and materials phenomena controlling electrochemical processes that will lead to a dramatic improvement in the performance of electrical energy storage devices, notably batteries.*

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.

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.

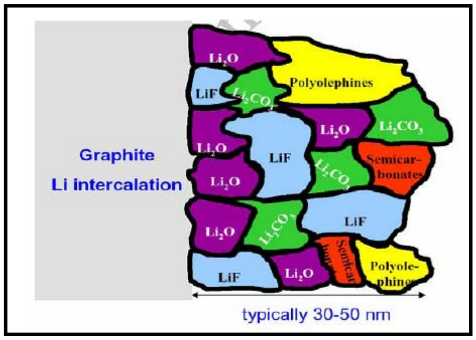


Figure 1. Schematic depiction of a solid-electrolyte interface ("SEI" layer)

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 designing and evaluating three-dimensional electrode/electrolyte interfaces using novel architectures, nano-phase materials, and tailored surfaces. With the goal of investigating and ultimately controlling the SEI, this task combines experimental studies with 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

The central focus of this subtask is the characterization of processes associated with materials lithiation that ultimately limit the performance of energy storage materials through the application of advanced *in-situ* characterization tools coupled with high-level theory. Phenomena of interest include materials strain due to lattice expansion due to Li incorporation, the role of lateral heterogeneities, the breakdown of solvent molecules at elevated potentials leading to the formation of an SEI, and the role of additives and passivating layers in stabilizing the interface and 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.

Center for Electrical Energy Storage (CEES)	
Argonne National Laboratory	M. M. Thackeray (Director), K. Amine, L. A. Curtiss, J. W. Elam, P. Fenter, J.P. Greeley, N. Markovic
University of Illinois, Urban-Champaign	A. A. Gewirth, D. D. Dlott, J. S. Moore, R. G. Nuzzo, N. R. Sottos, S. R. White
Northwestern University	H. H. Kung, M. J. Bedzyk, M. C. Hersam, C. Wolverton

Contact: Michael Thackeray; thackeray@anl.gov; (630)-252-9184;
http://www.anl.gov/energy-storage-science/

Center for Bio-Inspired Solar Fuel Production (BISfuel)

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.

Society's heavy reliance on fossil fuels is not sustainable, leads to a variety of geopolitical problems, and contributes to climate change. Given the size of the energy economy, sunlight is the most promising alternative energy source as it has the capacity to readily fill all energy needs. 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.

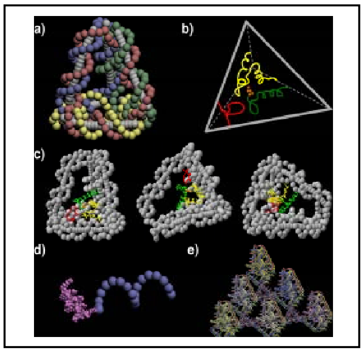
Fuel production requires not only energy, but also a source of electrons and precursor materials suitable for reduction to useful fuels. The immense magnitude of the human energy requirement dictates that the most reasonable source of electrons is water oxidation. Suitable precursor materials are hydrogen ions from water oxidation (for hydrogen gas production) and carbon dioxide (for reduced carbon fuels).

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. Thus, photosynthesis is a practical, time-tested natural example of large-scale solar fuel production.

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

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

One approach to water oxidation complexes is based on a unique, self-assembling, engineered DNA nanostructure that organizes short synthetic peptides arranged in a manner analogous to those in the natural oxygen-evolving complex (see box at right). These peptides are being used to construct a metal-ion-based catalytic site similar to the natural one using assembly methods found in photosynthesis. In a second method, peptide-based water-soluble analogs of the natural photosynthetic oxygen-evolving complex are being sought. Other approaches, including nanoparticulate metal oxide catalysts are being studied as well. The DOE ALS in Berkeley and other DOE National



Laboratory resources are being used for X-ray, XAFS and XANES characterization of the artificial water oxidation (and proton reduction) catalysts.

Hydrogen production catalysts under development are based on natural hydrogenase enzymes. Iron-containing catalytic sites and iron-sulfur sites for storing reduction equivalents are being organized into functional catalysts using metal nanoparticles or other methods and linked to transparent electrodes.

New transparent, nanostructured, high-surface-area semiconducting metal oxide materials are being constructed to serve as functional frameworks for organizing the 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 requires 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 are being used in order to permit electrochemical testing of components 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 challenge for fundamental and applied science.

While pursuing this ambitious goal, the Center is uncovering 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 so that it can better fill humanity's needs.

The project requires close cooperation among scientists from a wide variety of disciplines, including biology, biochemistry, molecular biology, synthetic organic chemistry, inorganic and bioinorganic chemistry, photochemistry and photophysics. Each Center research subtask focusing on a component of the final system is itself multidisciplinary, and all subtasks must work together to assure that the components being developed will ultimately function in the same device. Thus, the Center provides an excellent training opportunity for students and postdoctoral associates who are interested in alternative energy or other multidisciplinary fields.

Center for Bio-Inspired Solar Fuel Production	
Arizona State University	Devens Gust (Director), J.P. Allen, P. Fromme, G. Ghirlanda, A.K. Jones, Y. Liu, A. L. Moore, T. A. Moore, K. Redding, D.-K. Seo, H. Yan

Contact: Devens Gust
Regents' Professor
gust@asu.edu
480-965-4547
http://solarfuel.clas.asu.edu/

Center for Interface Science: Solar Electric Materials (CISSEM)
EFRC Director: Neal R. Armstrong
Lead Institution: University of Arizona

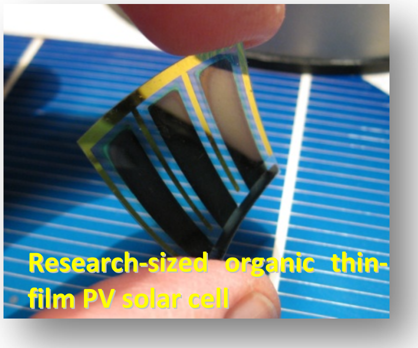
Mission Statement: CISSEM's mission is to advance the understanding of interface science underlying solar energy conversion technologies based on organic and organic-inorganic hybrid materials; and to inspire, recruit and train future scientists and leaders in the basic science of solar electric energy conversion.


CISSEM Interface-to-Face Research Conference, 2010

CISSEM was established in August 2009 under the Directorship of Prof. Neal R. Armstrong at The University of Arizona (UA). UA is teamed with the Georgia Institute of Technology, the National Renewable Energy Laboratory (NREL), Princeton University, and the University of Washington in a five-year $15M program involving seventeen principal investigators; with more than sixty graduate students, postdoctoral research associates, research scientists, and staff involved with the center. Research at CISSEM is focused on understanding, modifying, and controlling what happens in emerging thin-film photovoltaic (PV) technologies at nanometer length scales (one nanometer is about 1/100,000 of the width of a human hair) in regions called "interfaces" that are formed where different materials are brought into contact with each other. CISSEM combines state-of-the-art facilities, leading researchers, and enthusiastic students in the interface science of solar electric energy conversion, building the scientific foundation and training the future energy scientists required to develop abundant, clean, and economical energy conversion technologies for the 21st century.

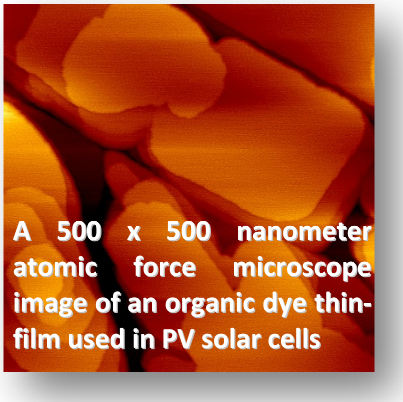
Interfacial processes are the thrust of our collaborative and synergistic efforts, in particular at organic/oxide, organic/metal and oxide/oxide interfaces. The chemical and physical processes that occur at these interfaces can control the efficiency, lifetime, and manufacturability of thin-film PVs, and so must be understood and improved to support the desired growth of PV technologies and the U.S. renewable energy portfolio. CISSEM is undertaking an integrated, multi-investigator effort to understand how interface composition and morphology at the molecular level can be controlled and improved to affect thin-film PV performance through the following four Major Goals:

1. Develop new theories to better understand charge transfer between organic semiconductors, oxides, metals, and emerging nontraditional conductors.
2. Develop new methodologies for the characterization of the atomic and molecular composition of interfaces, and new approaches for the nanoscale characterization of electrical and electrochemical properties of these interfaces.
3. 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.
4. Apply our understanding of nanoscale organic/oxide, organic/metal and organic/organic interfaces to existing and future solar energy conversion photovoltaic platforms.


Research-sized organic thin-film PV solar cell

CISSEM is:

- A multi-investigator center addressing the science of interfacial processes that limit efficiencies and lifetimes in emerging solar electric energy conversion technologies, requiring characterization and control of these processes at nanometer length scales.
- Developing and characterizing hybrid materials and robust interfaces, involving oxides, metals, semiconductors, and polymers; to help build the scientific foundation for low-cost, area-scalable, thin-film PV technologies and eventually enable the U.S. to reach terawatts of solar energy production at a $1/watt (peak).
- An integrated synergistic EFRC approach to tackle complex problems; combining the technology and expertise of four universities and NREL, the U.S. federal laboratory "dedicated to the research, development, commercialization and deployment of renewable energy and energy efficiency technologies."
- An outstanding training opportunity for future energy scientists and leaders through engaging the array of research facilities and expertise at CISSEM's universities and NREL.


A 500 x 500 nanometer atomic force microscope image of an organic dye thin-film used in PV solar cells

The CISSEM research program creates new scientific understandings of interfaces relevant to many complementary energy conversion systems, including thin-film PVs, energy storage, solar photocatalysis, and solid state lighting. CISSEM is a national resource in interface science with an impact that reaches beyond solar electric energy conversion.

Expanding the reach and the impact of our EFRC through UA's Energy Science Group (ESG) http://energysciencegroup.ning.com/

Center for Interface Science: Solar Electric Materials (CISSEM)	
The University of Arizona	Neal R. Armstrong (Director), Dominic V. McGrath, Oliver L. A. Monti, Jeanne E. Pemberton (Associate Director), S. Scott Saavedra (Associate Director)
Georgia Institute of Technology	Jean-Luc Brédas, Samuel Graham, Bernard Kippelen (Associate Director), Seth R. Marder (Associate Director)
National Renewable Energy Laboratory (NREL)	Joseph J. Berry, David S. Ginley (Associate Director), Dana C. Olson
Princeton University	Antoine Kahn
University of Washington	David S. Ginger

Contact: Robin E. Richards
Assistant Director, Science and Business Operations
efrc@cbc.arizona.edu
http://solarinterface.org

*Updated April 2012

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
U. of Illinois	Anthony J. Leggett Laura Greene Dale VanHarlingen Peter Abbamonte Jim Eckstein

Contact: J. C. Seamus Davis
jcdavis@ccmr.cornell.edu
607-220-8685
http://www.bnl.gov/energy/ces/

Light-Material Interactions in Solar Energy Conversion (LMI)

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 frequency conversion (upconversion and downconversion) using sunlight, using, 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

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:

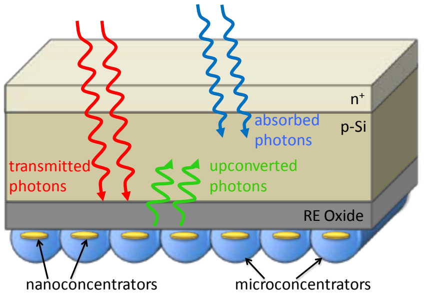


Figure 1. Photon upconversion process.

The RG-1 "***Frequency Conversion (Upconversion/ Downconversion)***" 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 "***Metallodielectric 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

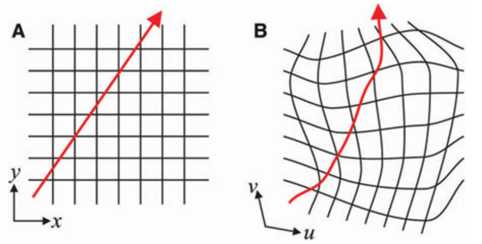


Figure 2. Principle of transformation optics. (a) light ray travelling in vacuum; (b) in coordinate-transformed medium.

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.

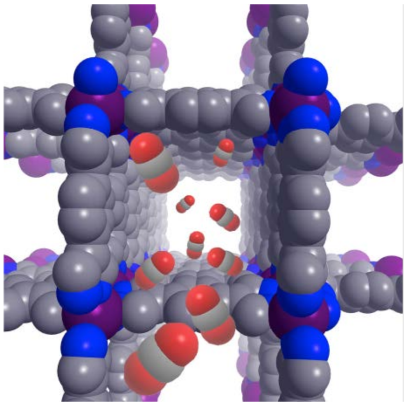
Light-Material Interactions for Energy Conversion (LMI)	
California Institute of Technology	Harry A. Atwater (Director), N.S Lewis and O.J. Painter
Lawrence Berkeley National Laboratory	A.P. Alivisatos, E. Yablonovitch, X. Zhang
University of Illinois	P. Braun, J.A. Lewis, R. Nuzzo, J.A. Rogers

Contact: Jennifer Blankenship, LMI EFRC Administrator; jblank@caltech.edu ; 626-395-3330
http://lmi.caltech.edu/

Center for Gas Separations Relevant to Clean Energy Technologies (CGS)
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 major 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 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 to 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.

Center for Gas Separations Relevant to Clean Energy Technologies	
University of California, Berkeley	Berend Smit, Jeffrey Long, Jeffrey Reimer, Ting Xu
Lawrence Berkeley National Laboratory	Maciej Haranczyk, Brett Helms, Blandine Jérôme, Jeffrey Kortright, Jeffrey Neaton, Frantisek Svec, Simon Teat, Omar Yaghi
University of California, Davis	Giullia Galli
University of Minnesota	Laura Gagliardi
National Energy Technology Laboratory	David Luebke

Contact: Blandine Jérôme
Bjerome@lbl.gov
http://www.cchem.berkeley.edu/co2efrc/

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 rationally design, synthesize and test revolutionary new materials for sustainable solar energy generation, electrochemical energy storage, and greenhouse gas capture. Achieve transformational improvements in materials performance via controlling material structure on the nanoscale using selectively designed, abundant and inexpensive molecular building blocks.

MEEM 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.

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. The nanometer-scale structure of conjugated polymers and polymer blends will be controlled 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.

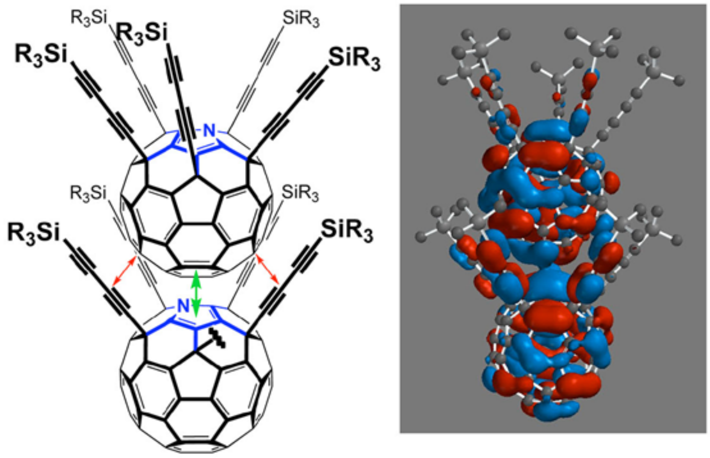


Figure 1. So-called “shuttlecock” molecules based on the heterofullerene $C_{59}N$ with phenyl “feathers” optimized for ideal close contacts within stacks. These molecules are expected to self-assemble into one-dimensional wires, enhancing the efficiency of charge separation and carrier transport in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

Supercapacitors based on inexpensive metal oxides present an attractive option for large-scale energy storage from intermittent sources, such as wind and solar, but their widespread adoption is hampered by efficiencies that are significantly lower than theoretical estimates. Elucidating the microscopic factors that limit the performance of oxide-based electrochemical supercapacitors is a major research direction in MEEM. 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.

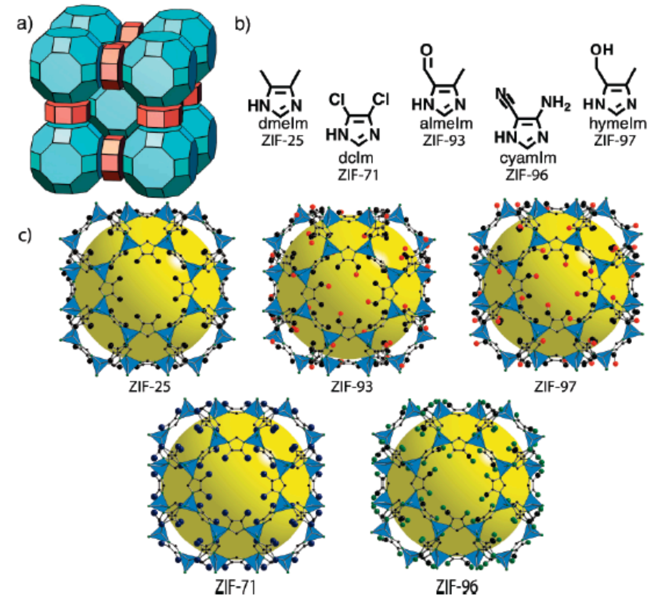


Figure 2: Crystal structures of isoreticular ZIFs based on ZIF-93, space group # 229 (Im3m). In spite of the close similarities in their crystal structures, these materials exhibit significantly different CO2 adsorption properties (Morris et al. *J. Am. Chem. Soc.* (2010) vol. 132 (32) pp. 11006-11008).

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 surface area (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 focuses on discovering the correlation between the structure of a ZIF and its performance, identifying the adsorptive sites within the pores of ZIFs, understanding diffusion of carbon dioxide within ZIFs, and developing strategies for optimizing the performance of ZIFs to affect highly selective and rapid carbon separation.

Research trusts are integrated on the basis of creating innovative nanometer-scale material architectures to achieve fast, highly efficient charge and mass transfer, and specifically tailored thermodynamics of charge and mass storage.

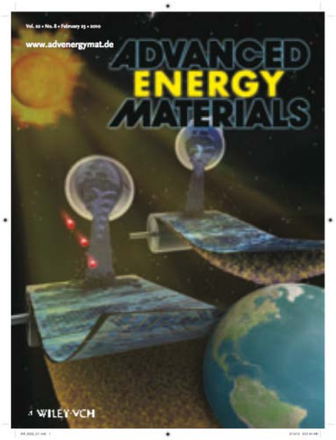
Molecularly Engineered Energy Materials (MEEM)	
University of California, Los Angeles	V. Ozolins (Director), B. N. Dunn (Assistant Director), Y. Lu, D. Neuhauser, L. Pilon, Y. Rubin, B. J. Schwartz, S. H. Tolbert
University of California, Berkeley	M. D. Asta
University of Kansas	B. Laird
National Renewable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

Contact: Vidvuds Ozolins
Professor, Dept. of Materials Science & Engineering
vidvuds@ucla.edu
(310) 267-5538
http://meem.ucla.edu

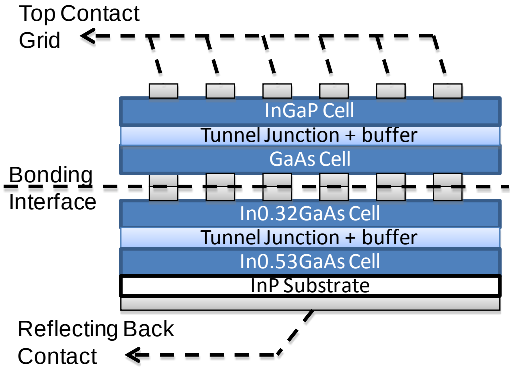
Center for Energy Efficient Materials (CEEM)
EFRC Director: John Bowers
Lead Institution: University of California, Santa Barbara

Mission Statement: To discover and characterize new materials which control the interactions between light, electricity, and heat at the nanoscale, and to apply them to achieve higher efficiencies in photovoltaic solar cells, solid-state lighting, and thermoelectric devices for converting heat into electricity.

The Center's research program is highly cross-disciplinary and is organized into teams, each having extensive expertise in materials growth, characterization, theoretical modeling; and device design, fabrication, and characterization. These collaborative teams encompass multiple disciplines and multiple institutions: UC Santa Barbara (lead), UC Santa Cruz, Harvard University, the National Renewable Energy Laboratory, and the Los Alamos National Laboratory. Although the center's primary focus is basic research, its longer-term objective is to transfer new materials and devices into the commercial sector to impact the nation's need for sustainable energy resources.



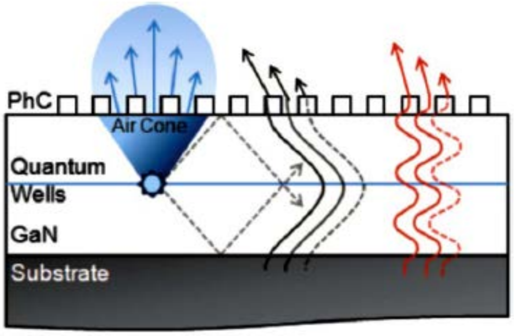
Research in **Plastic Solar Cells** emphasizes new conjugated materials that incorporate molecular design elements to optimize concurrently absorption and charge transport properties. Additives are included in the film casting solution to control the morphology of light collecting and charge generating materials to circumvent the current need for thermal annealing or slow solvent evaporation procedures. Detailed characterization of interfaces, local molecular organization, and charge mobilities at the nanoscale provide more precise control of bipolar heterojunctions, thus improving the reproducibility of their fabrication and their optoelectronic performance. The goal of this synergistic multidisciplinary approach is to demonstrate the feasibility of stable and efficient solar cells manufacturable by printing and coating technology enabling low-cost solar energy conversion.



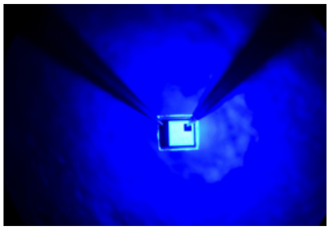
High Efficiency Solar Cells using novel materials are being developed for applications suitable for high efficiency concentrator applications. Specifically, photovoltaics using thin films of the InGaN family of materials from GaN to InN offer the possibility of achieving a full-spectrum solar cell. These materials can be grown either on the Ga-face, N-face or the non-polar surfaces of GaN to maximize PV efficacy. A research goal is to utilize the N-face of GaN to develop polarization-free PV, which are advanced MIS cells using the reverse polarization of the AlGaN wideband gap layer. This enhances the open-circuit voltage with a minimum decrease in short-circuit current. We are also developing the technology of nano-GaN materials as a promising pathway toward large-area solar cells on inexpensive substrates and are developing multi-junction InGaN cells using tunnel junctions and wafer bonding and applying these to nano-GaN solar cells.

Bio-inspired and nano-structured materials are being explored to advance our understanding and control of heterogeneous materials engineered at the nanoscale for applications to improve the performance and cost of photovoltaic devices. Using both inorganic and biological templates to control nanostructure, our goal is to optimize separately the distinctive length scales that characterize photovoltaic operation relating to excitation, charge separation, carrier extraction, and recombination.

Semimetal nanoparticles in semiconductors are being used to develop **novel thermoelectric devices** that have higher Seebeck coefficients and electrical conductivity, and reduced electronic and lattice thermal conductivities. We are exploring a wide range of new materials, including rare earth bismuthides, antimonides, phosphides, nitrides, and arsenides and clathrates. Our calculations show that ZT > 2 is possible, and the design can be optimized for a particular temperature range while a stack of such layers is optimized for kW generation from large temperature differences. We target two types of nanostructured TE materials: (1) bulk systems with nanostructure-modulated heterostructures made by incorporating metallic nano-domains into a semiconducting matrix, and (2) packaged, highly oriented nanowire arrays which can be assembled on a large scale with electrochemical control of composition and impurity levels, and with well-defined nanowire dimensions and sculptured nanoscale geometries.



The objective of the Center's **Solid-State Lighting** research is to address the basic materials science and engineering required to achieve all semiconductor-based white-light sources with output greater than 300 lumens/watt, corresponding to greater than 80% wall-plug efficiency. We intend to achieve these goals by: (1) pioneering the application of photonic-crystals to enhance the extraction efficiency of light-emitting diodes based on embedded two-dimensional air-gap photonic-crystals; (2) control and elucidation of the carrier loss mechanisms on polar and nonpolar/semipolar GaN LEDs including a detailed understanding of all radiative and nonradiative pathways; and (3) developing full-spectrum lighting using an all semiconductor-based emission region.



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. Stemmer, S.P. DenBaars, J. Speck, C. Van de Walle, T.Q. Nguyen, U.K. Mishra, D. Morse, M. Moskovits, C. Weisbuch, C. Palmstrom, M. Chabinyc
National Renewable Energy Laboratory	D. Friedman, D. Ginley
Los Alamos National Laboratory	S. Tretiak
Purdue University	A. Shakouri

Contact:

John Bowers, Director
bowers@ece.ucsb.edu
(805) 893-8447
www.ceem.ucsb.edu

David Auston, Executive Director
auston@iee.ucsb.edu
(805) 893-3376
www.ceem.ucsb.edu

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.

The critical shortage of abundant, affordable, and clean energy calls upon novel materials that are superior to any known material existing today with extreme properties for energy production, storage, conversion, and transfer. The extreme pressure-temperature (*P-T*) environments present a vast, unexplored, fertile ground to search for transformative materials and phenomena. The Center approach is essential for advancing the high-pressure technology and allying the high-pressure community efforts to accelerate breakthroughs in the energy technologies.

High pressure categorically alters physical properties of phonon, electron, and structure and chemical properties of bonding, reactivity, and kinetics. Pressure pushes materials across conventional barriers between insulator and superconductor, fluid and solid, molecular and extended frameworks, and the vigorously reactive and the inert. The extreme *P-T* studies provide a new route towards discovering new materials with enhanced performance for 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 the nation's leading scientists with complementary expertise in high-pressure science and technology, theory and experimentation, physics, chemistry, geoscience, and materials science. Efree develops the critical 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 enabling platform, the EFree management directs and monitors dozens of research projects aiming for transformational advances in three thrust areas.

1. Novel Chemical Energy Under Extreme P-T – Pressure drastically changes chemical speciation, dissolution, reactivity, combustion, catalysis, absorption, photochemistry, and electrochemistry. Pressure may create dozens of novel phases with very different properties in an average chemical system; many of them may be quenchable and may carry potential applications for energy generation, storage and transportation. The interest in high-pressure hydrogen has recently extended well beyond the elemental forms to encompass hydrogen-containing molecular alloys and compounds for hydrogen storage applications. EFree conducts a broad-based research program that includes work on the elemental states and those with hydrogen in chemical compounds, where results in one area enhance work in the other.

2. 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. Pressure strongly effects the emergent properties as well as ordinary electro-magnetic materials, including high-temperature superconductivity, topological insulator, charge- and orbital-density waves, electronic phase separation, magneto-capacitance, multi-ferroics, spintronics, , Mott insulatoion, heavy fermions, colossal magneto-resistivity, polar energy materials, and quasi low-dimensional materials, thus addressing problems ranging from efficient charge injection in photovoltaic devices to lossless electrical transmission over superconducting lines. Pressure-tuning plasmons, excitons, and electron dynamics are providing the fundamental information necessary for the grand challenge of controlling materials processes at the level of electrons.

3. Novel Nanophase, Mesoporous, Amorphous and Structural Energy Materials Under Extreme P-T – EFree addresses the underlying origin of pressure-induced transitions between crystalline and amorphous materials, and the creations of nanoscaled structures and orders. The dimensionality and size-scale of these materials are closely related to their applications for light emission, catalysis, filtering, membrane, etc. and potentially impact on energy efficiency, production, utilization, and storage. EFree applies variable high-*P, T,* and strain rate to synthesize new structural materials such as diamond, cBN, and tough lightweight carbon-based materials, and to study their response and resistance under extremely harsh *P-T* and chemical environments.

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. 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 of Washington	H.K. Mao (Director), R.J. Hemley (Associate Director), M. Baldini, R. Boehler, X.J. Chen, R.E. Cohen, Y. Fei, A.F. Goncharov, S. Gramsch, M. Guthrie, Z. Liu, G. Shen, V. Struzhkin, L. Wang, W. Yang
Argonne National Laboratory	G. Srajer
Brookhaven National Laboratory	Y. Cai
California Institute of Technology	B. Fultz
Cornell University	N.W. Ashcroft, R. Hoffmann, W. Bassett
Florida International University	J. Chen
Lawrence Livermore National Lab	J.C. Crowhurst, M.R. Armstrong
Lehigh University	K. Landskron
Missouri State University	R.A. Mayanovic
Oak Ridge National Laboratory	C. Tulk
Pennsylvania State University	J.V. Badding
Stanford University	W.L. Mao, C.C. Kao
University of Texas at Austin	J. Lin

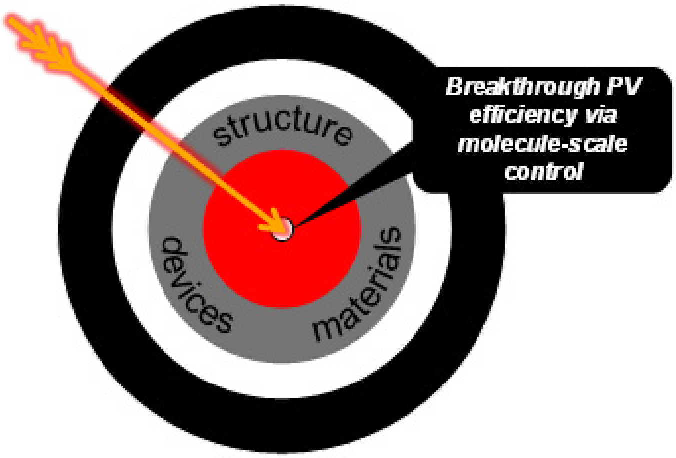
Contact: Ho-kwang Mao
Director of EFree
mao@gl.ciw.edu
(202)478-8960 (office)
https://efree.gl.ciw.edu/

Re-Defining Photovoltaic Efficiency Through Molecule Scale Control (RPEMSC)

EFRC Director (s): James Yardley; Tony Heinz; Louis Brus

Lead Institution: Columbia University

Mission Statement: The Columbia EFRC will create critical enabling technology which will redefine thin film photovoltaic efficiency through development of fundamental understanding based upon molecule-scale control of the key steps in the photovoltaic process for 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 the efficiency of inexpensive solar cells toward 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.

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 photophysical processes in these materials, using modern tools of Nanoscale science including ultrafast and single molecule spectroscopies. We are studying the structure of interfaces of new and novel thin film semiconductor materials with other semiconductors as well as with metals. Bases on these interfaces, we are correlating the charge transport characteristics at interfaces with the observed structure. 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 are building 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. We are examining the efficacy of new carbon-based conductor materials including graphene for use as transparent conducting materials for efficient extraction of charge from thin film photovoltaic devices. These activities merge to allow us to fabricate new devices and device structures for direct determination of photovoltaic characteristics in working devices. One example shown in Figure 1 is a novel "transparent" solar cell device using transparent graphene electrodes for both cathode and anode.

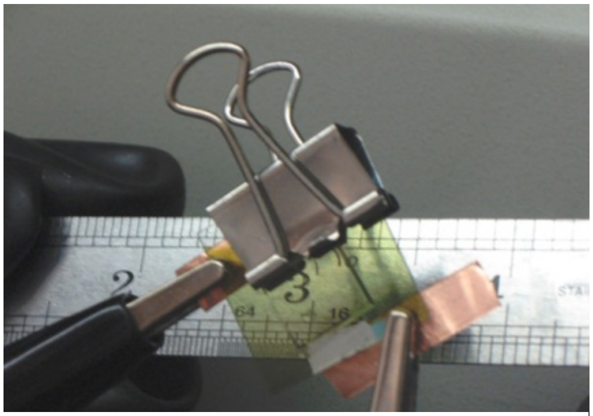


Figure 1. Transparent photovoltaic cell using graphene for both anode and cathode.

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. In addition we are exploring theoretically generic concepts for carrier multiplication processes. This will allow us to establish a quantitative and predictive theory for MEG and related carrier multiplication concepts. This theory will guide our experimental program in terms of systems under study and materials used in these systems.

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, Luis Campos, George Flynn, Irving Herman, James Hone, Philip Kim, Ioannis Kymissis, Colin Nuckolls, Richard Osgood, Jonathan Owen, David Reichman, Kenneth Shepard, Michael Steigerwald, Latha Venkataraman, Chee Wei Wong
Purdue University	Ashraf Alam
University of Texas	Xiaoyang Zhu
Brookhaven National Laboratories	Charles Black, Mark Hybertsen

Contact: James T. Yardley
Professor, Electrical Engineering
jy307@columbia.edu
212-854-3839
www.cise.columbia.edu/efrc/

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

Mission Statement: The 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.

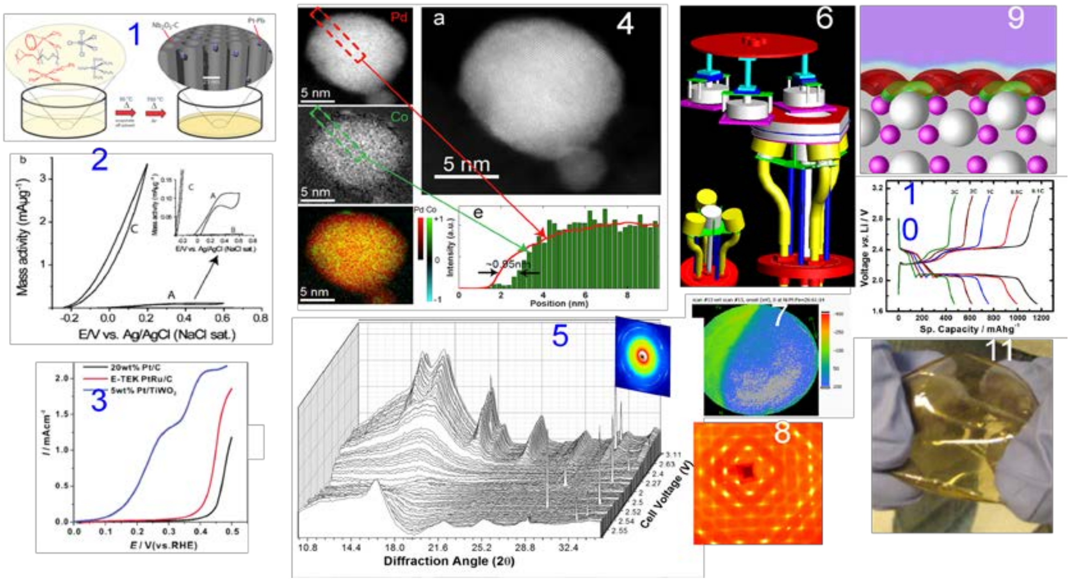


Figure 1

The aim of the Energy Materials Center at Cornell is to achieve a fundamental understanding of the effects of the nature, structure, and dynamics of these interfaces on energy generation, conversion and storage with emphasis on fuel cells and batteries. The center integrates the synthesis of nanostructures (Fig. 1: 1) as catalysts and catalyst supports for fuel cell applications (Fig. 1: 2,3), the design of novel alkaline membranes (Fig. 1: 11), the synthesis and characterization (with atomic precision and resolution) of core/shell catalysts (Fig. 1: 4), the electrochemical (Fig. 1: 10) and in-situ characterization, via x-rays (Fig. 1: 5, 8), of battery materials, along with combinatorial high throughput methods (Fig. 1: 6) and screening as well as computational studies (Fig. 1: 9). The knowledge-base emerging from these efforts will guide the synthesis of improved materials and the development of novel tools and testing capabilities that will provide *in-situ* spatiotemporal characterization over the range of conditions in which the appropriate technologies are intended to operate.

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

Contact: Héctor D. Abruña
Professor
hda1@cornell.edu
(607) 255-4720
http://www.emc2.cornell.edu/

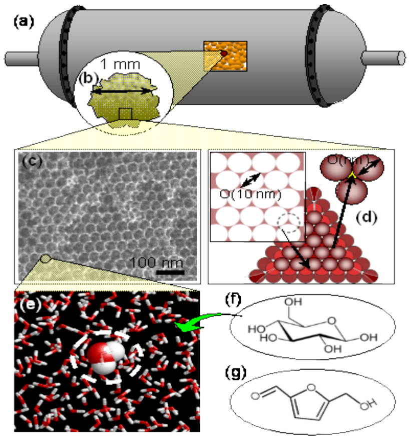
Catalysis Center for Energy Innovation (CCEI)
EFRC Director: Dion Vlachos
Lead Institution: University of Delaware

Mission Statement: Develop innovative heterogeneous catalytic technologies for future biorefineries and to 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 mainly focuses 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 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 and 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 develops 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 is central for in situ catalyst characterization of the CCEI catalysts.

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, students, and the public.

Catalysis Center for Energy Innovation (CCEI)	
University of Delaware	Dion Vlachos (Director), Mark A. Barteau, Douglas J. Buttrey, Stavros Caratzoulas, Prodromos Daoutidis, Weihau Deng, Douglas J. Doren, Thomas Epps, Feng Jiao, Michael T. Klein, Kelvin H. Lee, Raul F. Lobo, Giannis Mpourmpakis, Vladimiros Nikolakis, Stanley I. Sandler, Donald Watson, Yushan Yan
University of Pennsylvania	Raymond J. Gorte, John M. Vohs
University of Massachusetts	Paul J. Dauenhauer, Wei Fan
University of Minnesota	Aditya Bhan, Michael Tsapatsis
Lehigh University	Mark A. Snyder
Brookhaven National Laboratory	Anatoly I. Frenkel
California Institute of Technology	Mark E. Davis
Princeton University	Bruce E. Koel
Columbia University	Jingguang G. Chen
Massachusetts Institute of Technology	Yuriy Román
University of Wisconsin – Madison	George W. Huber

Contact: Dionisios (Dion) G. Vlachos
CCEI Director
vlachos@udel.edu
(302) 831-2830
www.efrc.udel.edu

Center for Advanced Biofuel Systems (CABS)
Jan Jaworski, Director
Donald Danforth Plant Science Center

Mission Statement: 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 identify kinetic and thermodynamic constraints in photosynthetic and lipid metabolism that limit the accumulation of biomass and oil in algae and oil seed plants. To relieve these metabolic constraints, we will 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 novel hydrocarbons required to meet commercial fuel standards. These strategies will be informed by comprehensive metabolic flux analyses of select algal and oil seed plants. Using strategies informed by computational models we will develop engineered organisms with enhanced biofuel production. What distinguishes our approach from many others is that we integrate all aspects of metabolism, from energy conversion in photosynthesis through end product production.

The technologies we will employ to address our objectives include:

1) Development of analytical and computation tools and metabolic flux models to direct engineering strategies to enhance biofuel production. Drs. Hicks, Schachar-Hill and 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 rate-limiting processes to increase metabolic flux. Drs. Sayre, Kutchan, Jaworski and Yu will develop new enzyme complexes to enhance and direct flux in existing networks as well as introduce novel metabolic pathways to channel reducing equivalents generated from the photosynthetic light reactions through the Calvin cycle to enhance oil and hydrocarbon 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. Dr. Wang will characterize and manipulate transcription factors involved in oil accumulation. Dr. Yu will focus on metabolic channeling and protein-protein interactions of multi-enzyme complexes involved in the fatty acid and lignin biosynthetic pathways.

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

5) Dr. Terry Woodford-Thomas directs our outreach and educational efforts to inform the public about the challenges facing sustainable energy production and the efforts of CABS in meeting those challenges.

Center for Advanced Biofuel Systems (CABS)	
Donald Danforth Plant Science Center	Jan Jaworski (Director), Toni Kutchan, Sam Wang,Oliver Yu, Leslie Hicks, Terry Woodford-Thomas
Michigan State University	Yair Schachar-Hill
University of Missouri – St. Louis	Sam Wang
New Mexico Consortium/Los Alamos National Laboratory	Richard Sayre
Washington State University	David Gang
University of Nebraska	Edgar Cahoon

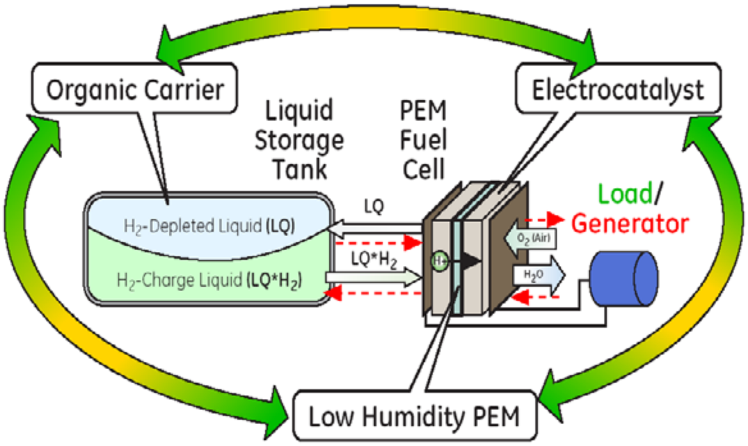
Contact: Jan Jaworski
Director, Center for Advanced Biofuel Systems
jjaworski@danforthcenter.org
(314)587-1621
http://www.danforthcenter.org/cabs/

Center for Electrocatalysis, Transport Phenomena, and Materials (CETM) 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, the catalyst promising leads from among the following classes of catalyst will be explored: i) catalysts for electrohydrogenation of CO_2, ii) 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 water-free 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.

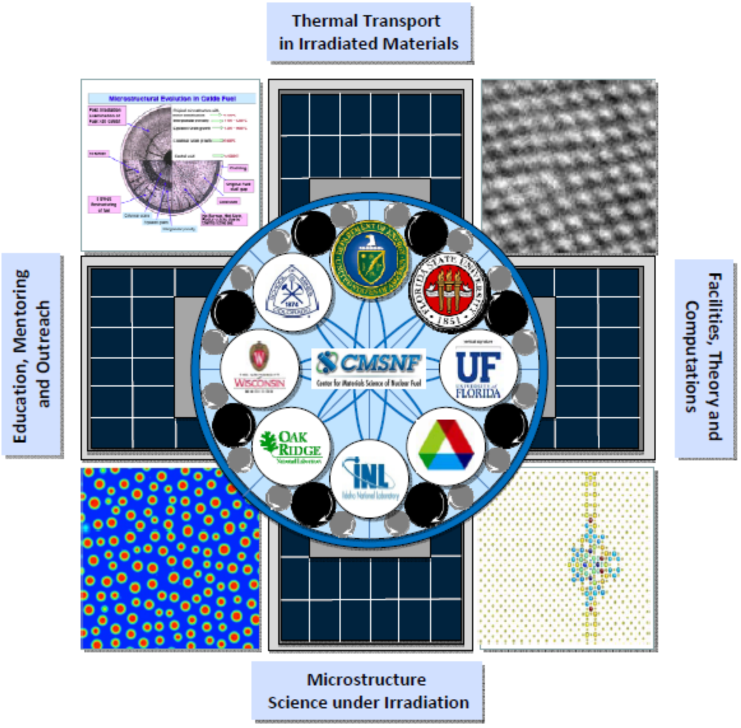
Center for Electrocatalysis, Transport Phenomena, and Materials (CETM) for Innovative Energy Storage	
General Electric Global Research	G.L. Soloveichik (Director), T. Miebach (assistant director), D. Simone, G. Yeager, J. Stein, M. Doherty, L. Krishnan, T. Lam, A. Peters, M. Rainka
Yale University	R.H. Crabtree, V.S. Batista
Stanford University	C.E.D. Chidsey, R. Waymouth
Lawrence Berkeley National Laboratory	J.B. Kerr, J. Arnold, J. Reimer

Contact: Grigorii Soloveichik
soloveichik@crd.ge.com
(518) 387-7906
www.ge.com/efrc

Center for Materials Science of Nuclear Fuel (CMSNF)
EFRC Director: Todd Allen
Lead Institution: Idaho National Laboratory

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

Project Description: The research goal of the Center for Materials Science of Nuclear Fuel is to achieve a first-principles based understanding of the effects of irradiation on thermal transport in irradiated UO_2. Irradiation leads to materials degradation due to the production of non-equilibrium defects and formation of complex defect structures. Thermal transport in ceramic materials such as oxide fuels, which is dominated by a phonon mechanism, is significantly affected by lattice defects due to the alteration of the lattice dynamics. In order to understand how irradiation impacts thermal transport in this class of materials, it is required to investigate the collective mechanisms of interaction of phonons with the lattice defects that form under irradiation. There are two challenges in this regard; the first is to determine the dominant types of defects and defect configurations created by irradiation, and the second is to understand how these defect configurations interact with phonons, the carrier of heat in oxide fuels. The center's research thus integrates the physics of thermal transport in crystalline solids with microstructure science under irradiation.



At the Center for Materials Science of Nuclear Fuel, we integrate the physics of thermal transport in crystalline solids with the microstructure science under irradiation to understand the impact of irradiation on thermal transport in nuclear fuel. The Center thus introduces a new paradigm of basic research in the field of radiation materials science.

The center's research consists of two complementary themes. The first theme is ***microstructure science under irradiation***, which aims to characterize defects in irradiated UO_2 (our model fuel) both computationally and experimentally, and provide all information required to investigate thermal transport in the defective material. The framework of non-linear dynamics of irradiation-driven materials is used to develop a generalized mesoscale phase-field model for the irradiation-induced disorder and microstructure evolution, which will furnish the defect state impacting thermal transport. The second theme, ***thermal transport in irradiated fuel***, focuses on first-principles computational modeling of thermal transport in defective materials and on performing measurements at the same length scales. The thermal transport modeling is based on Boltzmann transport equation for phonons, which includes the physics of phonon scattering by irradiation-induced defects, as collected by experiments and atomistic scale modeling. The planned theoretical and experimental investigations all focus on understanding the mesoscale aspects of impurity segregation, lattice disorder and microstructure evolution and the effect of such materials imperfections on thermal transport at the same length scale.

The Center brings together a world-class multi-institutional team of experimentalists and computational materials theorists with unique modeling capabilities in both microstructure and thermal transport areas. The center's experimental effort, on the other hand, capitalizes on the unique capabilities at several 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 synthesis and 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 tying all of the experimental investigations to a true reactor environment. Indeed, the longer term vision of the Center beyond the current phase is to understand the in-pile thermal transport in fuel, both theoretically and experimentally, and to develop new predictive models that can be benchmarked against actual ATR fuel data.

Center for Materials Science of Nuclear Fuel (CMSNF)	
Idaho National Laboratory	Todd Allen (Director), David Hurley, Jian Gan, Xianmin Bai, Marat Khafizov, Jianguo Yu
Purdue University	Anter El-Azab
University of Florida	Michele Manuel, Simon Phillpot
Colorado School of Mines	Jianliang Lin
University of Wisconsin – Madison	Todd Allen
Oak Ridge National Laboratory	Ben Larson, Judy Pang

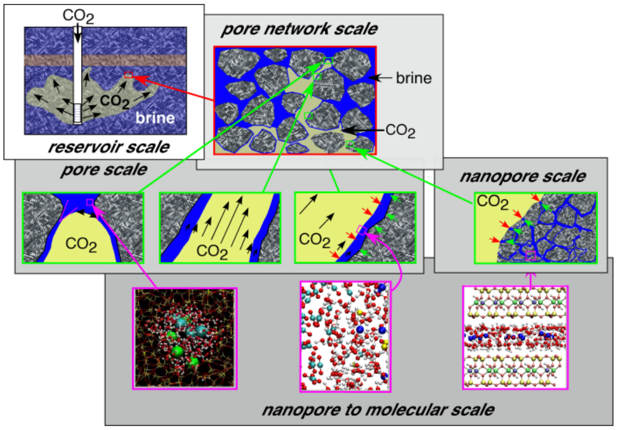
Contact: Todd Allen,
Scientific Director, ATR National Scientific User Facility
Idaho National Laboratory
allen@engr.wisc.edu
Tel. 608-265-4083
http://www.inl.gov/efrc

Center for Nanoscale Control of Geologic CO$_2$ (NCGC)

EFRC Director: Donald J. DePaolo
Lead Institution: Lawrence Berkeley National Laboratory

Mission Statement: To improve understanding of fluid-rock processes using a coordinated research effort focused on molecular- to pore scale phenomena, where major knowledge gaps exist for predicting macroscopic material properties and large scale fluid-rock dynamical behavior related to the injection and storage of CO$_2$ in subsurface reservoirs.

Technical Overview: The objective of the NCGC Center is to use new investigative tools*, combined with* experiments and computer simulations, 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$_2$. The objectives address fundamental science challenges related to far-from-equilibrium systems, nanoscale processes at interfaces, and emergent phenomena.



Unique BES experimental facilities at the primary work site, LBNL, together with facilities located at ORNL, 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.

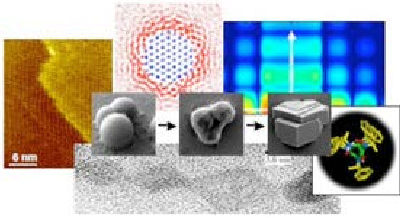
The specific overarching goals are to (1) establish, within 10 years, novel molecular, nanoscale, and pore-network scale approaches for controlling flow, dissolution, and precipitation in deep subsurface rock formations to achieve the efficient filling of pore space with injected supercritical CO$_2$, with maximum solubility and mineral trapping and near-zero leakage, and (2) develop a predictive capability for reactive transport of CO$_2$-rich fluid that is applicable for 100–1000 years into the future to enhance storage security and efficiency.

The major technological gaps to controlling and ultimately sequestering subsurface CO$_2$ can be traced to far-from-equilibrum processes that originate at the molecular and nanoscale, but are expressed as complex emergent behavior at larger scales. Essential knowledge gaps involve the effects of nanoscale confinement on material properties, flow and chemical reactions, the effects of nanoparticles, mineral surface dynamics, and microbiota on mineral dissolution/precipitation and fluid flow, and the dynamics of fluid-fluid and fluid-mineral interfaces. The construction of quantitative macroscale process models based on nanoscale process descriptions is a critical additional fundamental knowledge gap.

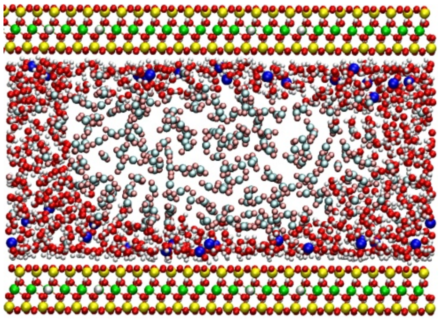
The efforts of the Center investigators are grouped into three Thrust Areas:

- Controlling Nucleation and Growth
- Nanopore Processes
- Emergent Processes

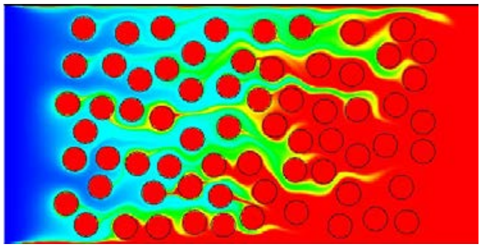
The three Thrust Areas represent groupings of investigators whose work in the Center will be directed at closely allied scientific challenges. However, there are a large number of cross connections within and between these Thrust Areas. The three Thrust Areas have three to six lead scientists, representing all of the institutions involved and constituting the management and scientific leadership of the Center.



Controlling Nucleation and Growth: Manipulating the dissolution, nucleation and growth of minerals in the subsurface requires a detailed understanding of these processes and how they are affected by the special characteristics of porous rock media. The objective of Thrust Area 1 is to develop that understanding at the molecular-level, define the role of microbial communities in mediating those processes in reservoir environments and to explore inorganic, biological and biomimetic methods of directing carbonate mineralization in the sub-surface.



Nanopore Processes: One of our major scientific challenges is to understand the behavior of carbon dioxide-rich aqueous solutions confined at high temperature and pressure in nanoporous matrices under geologic sequestration conditions. The goal of research under Thrust Area 2 is to provide a fundamental understanding of these confined carbon dioxide-aqueous solution mixtures using advanced experimental and computational methodologies to probe fluid behavior from molecular to pore scales.



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. Under these conditions, the strong coupling between flow, transport, and reaction may result in emergent structures and pattern formation that develop within the porous structure of the subsurface at scales ranging from the nano-pore and macro-pore all the way up to that of a sedimentary basin. These emergent dynamics must be understood in order to predict how CO_2 will behave when injected into the subsurface.

Center for Nanoscale Control of Geologic CO_2	
Lawrence Berkeley National Laboratory	D.DePaolo (Director), J. DeYoreo (Deputy Director/Thrust Area 1 Lead), I. Bourg (Thrust Area 2 Lead), C. Steefel (Thrust Area 3 Lead) Participants: C. Ajo-Franklin, J. Ajo-Franklin, J. Banfield, Y. Kim, S. Pride, G. Sposito, T. Tokunaga, D. Trebotich, J. Urban, G. Waychunas, J. Wan, S. Whitelam, L. Yang, R. Zuckerman
Lawrence Livermore National Laboratory	Technical Lead: R. Ryerson Participant: P. Weber
Massachusetts Institute of Technology	Technical Lead: D. Rothman
Ohio State University	Technical Lead: D. Cole
Oak Ridge National Laboratory	Technical Lead: G. Rother Participants: L. Anovitz, A. Chialvo, M. Gruszkiewicz, A. Stack, L. Vlcek
University of California-Davis	Technical Lead: A. Navrotsky
Washington University in St. Louis	Technical Lead: J-S. Jun

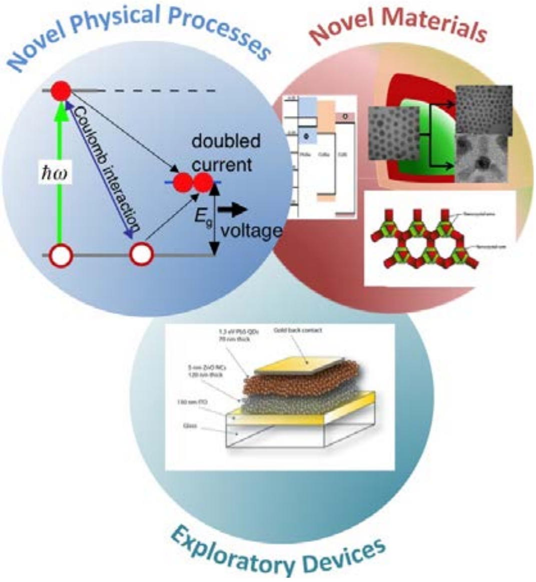
Contact: Donald J. DePaolo, DJDePaolo@lbl.gov, website: http://esd.lbl.gov/research/facilities/cncgc/

Center for Advanced Solar Photophysics (CASP)

EFRC Director: Victor I. Klimov
Lead Institution: Los Alamos National Laboratory

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

Technical Overview: 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 nanoscale 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:

1. *Novel physical phenomena for efficient capture and conversion of light into electrical charges via quantum confinement, plasmonic and photonic effects;*
2. *New means for efficient charge manipulation in nanoassemblies and proof-of-principle device structures that exploit the emergent physics of the nanoscale size regime;*
3. *Novel nanomaterials for probing and controlling the fundamental physics of the nanoscale size regime, and for applications in exploratory devices.*

Thrust 1. The new physical principles for light harvesting and conversion into electrical charges that are 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 control of excited state dynamics and Coulomb interactions in semiconductor heterostructures and semiconductor-metal hybrids. 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, nanoengineering approaches for controlling “hot-carrier” dynamics can allow one to increase the device photovoltage. Finally, 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.

Thrust 2. Effective exploitation of the unique properties of nanostructured materials in solar energy conversion, especially in utilizing multiple excitons or “hot electrons”, is contingent upon our ability to efficiently extract and transport carriers to charge collecting electrodes. To this end, the second Thrust explores charge separation and transport, as well as energy transfer, in engineered nanoassemblies.

Specific research topics include extraction of multiple charges, exciton transport in extended gradient structures, and the effects of semiconductor-metal interaction on energy transfer. This thrust also includes research into prototype Generation-III devices that demonstrate enhanced power conversion efficiency through utilization of novel nanoscale physics and novel architectures. These exploratory devices are specifically designed to harness the physical principles found in both discrete and simple extended structures and are used to elucidate key phenomena endemic to sequential increases in complexity, e.g., in progressing from a simple nanocrystal film to a multilayer device.

Thrust 3. The physics and device efforts depend critically on the availability of advanced nanomaterials, while at the same time producing insights crucial to identifying, and even designing, the next generation of desirable materials. The third Thrust seeks to push the envelope of nanomaterials synthesis to continuously approach the ideal behavior sought by physicists and device scientists, as well as to discover unique functionalities in new NCs and hybrid composite nanomaterials. Three main areas of research within this Thrust include developing high quality solution-processible NCs of solar-relevant bulk materials, exploring new motifs in shape-control and heterostructuring for “band engineering” of NCs, and creating unique multi-functional semiconductor-metal nanohybrids. A central, unifying theme across these efforts is the use of low-cost, scalable methodologies to produce high-quality materials amenable to solution-based processing.

Center for Advanced Solar Photophysics (CASP)	
Los Alamos National Laboratory	V.I. Klimov (Director), J.M. Pietryga, I. Robel, S. Tretiak
National Renewable Energy Laboratory	M.C. Beard (Associate Director), J.C. Johnson, J.M. Luther, N.R. Neale, A.J. Nozik
University of California, Irvine	M. Law, J.C. Hemminger
Rice University	N.J. Halas, P.J. Nordlander
University of Minnesota	U. Kortshagen
University of Colorado	D.M. Jonas
Colorado School of Mines	P.C. Taylor
George Mason University	A.L. Efros

Contact: Victor I. Klimov
klimov@lanl.gov
http://casp.lanl.gov
http://www.centerforadvancedsolarphotophysics.org

Center for Materials at Irradiation and Mechanical Extremes (CMIME)
EFRC Director: Amit Misra
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, the Center for Materials at Irradiation and Mechanical Extremes (CMIME), 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 focuses on *materials at irradiation and mechanical extremes*. 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 will develop 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 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.

Center for Materials at Irradiation and Mechanical Extremes (CMIME)	
Los Alamos National Laboratory	A. Misra (Director), Senior Personnel, I.J. Beyerlein, G.T. Gray, S.A. Maloy, B.P. Uberuaga, N. A. Mara, T.C. Germann, E.K. Cerreta, A.F. Voter, S.M. Valone, S. Luo, Q. Jia, D.A. Yarotski, A. Caro.
Carnegie Mellon University	Senior Personnel, A.D. Rollett
University of Illinois-Urbana Champaign	Senior Personnel, R.S. Averback, P. Bellon
MIT	Senior Personnel, M. J. Demkowicz
University of Nebraska	Senior Personnel, M. Nastasi

Contact: Amit Misra
Director
amisra@lanl.gov
(505) 667-9860
http://cmime.lanl.gov/

Center for Atomic-level Catalyst Design (CALCD)
EFRC Director: James Spivey
Lead Institution: Louisiana State University

Mission Statement: Our mission is to extend the current capabilities of three essential disciplines needed to design catalysts from first principles: (a) computational catalysts, (b) atomically precise synthesis, and (c) unambiguous characterization at the atomic scale. This will allow us to develop catalysts that achieve the highest possible activity and selectivity in energy conversion processes.

Rationale. 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 atom-by-atom (Fig. 1). Assuming other factors are constant (such as the complexity of the reaction), as the size of the active catalyst surface increases, the level of control over the atomic-level structure of the surface decreases, for example because defects are inevitably introduced in the preparation of the catalyst. However, a computational description of the working catalyst based on quantum mechanics becomes less realistic as the size of the catalyst surface increases (especially under reaction conditions), typically because we must make simplifying assumptions that cannot be easily verified. Although the absolute length scale representing the limits of computation or synthesis may vary for different metals and reactions, there is a gap in our ability to identify an ideal catalyst by computation and to then prepare and characterize it unambiguously with atomic-level precision (Fig. 2).

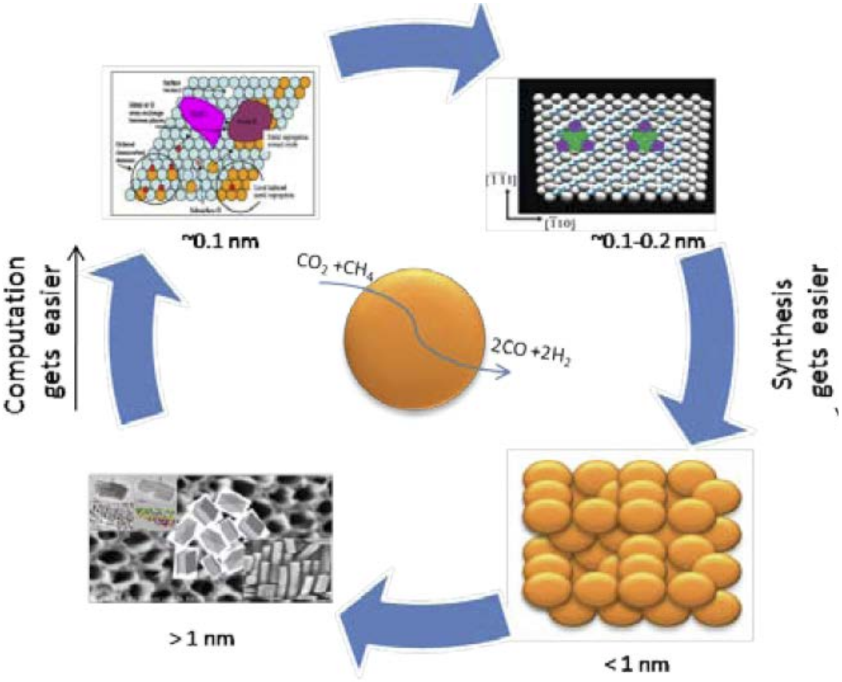


Fig. 1. Schematic representation of the degree of difficulty in computation and synthesis of catalysts.

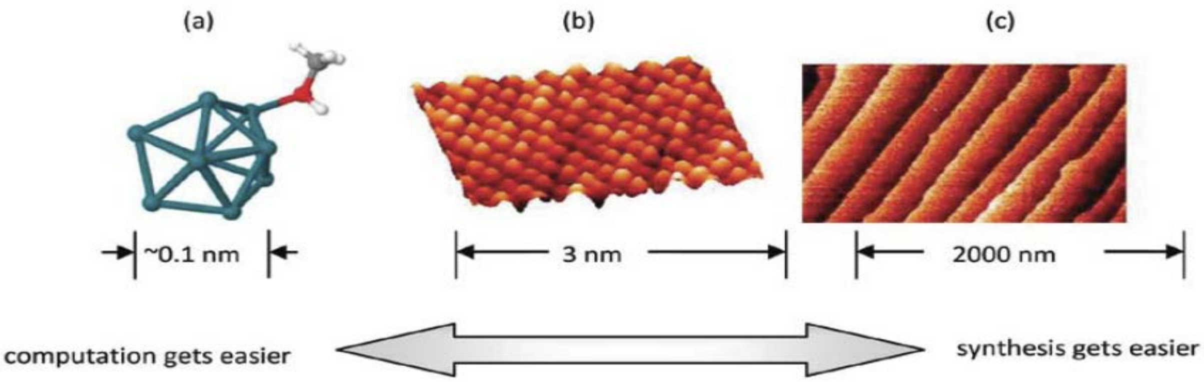


Fig. 2. Difficulty of computational and synthesis/characterization research vary in opposite directions with length scale; (a) CH_3OH on Rh_7 cluster (DFT model by D. Bruce, Clemson Univ.); (b) $Pt_{25}Rh_{75}$(100) Alloy 3-d topography (www.omicron.de); (c) Mono-atomic steps on SiO_2 layer - in UHV at T = 800K in AFM mode.

Approach. Our approach is two-fold; (a) extend the capabilities of current computational and synthesis/characterization tools and (b) use these tools to synthesize and characterize computationally designed catalysts. 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. 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. This approach is anticipated to challenge the current limits of both synthesis tools and computational techniques.

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, A. Roy
Clemson University	D. Bruce
Texas A&M University	M. Rosynek
Georgia Tech	D. Sholl
University of Utrecht, Netherlands	K. P. de Jong, P.E. de Jongh
University of Florida	S. Sinnott
Ohio State University	A. Asthagiri
Oak Ridge National Laboratory	Y. Xu
Vienna University of Technology	U.Diebold
Pennsylvania State University	M. Janik
Grambling State University	N. Seetala

Contact: *Ellen Stevens, Business Manager; 225-578-0058; esteve2@lsu.edu; www.efrc.lsu.edu*

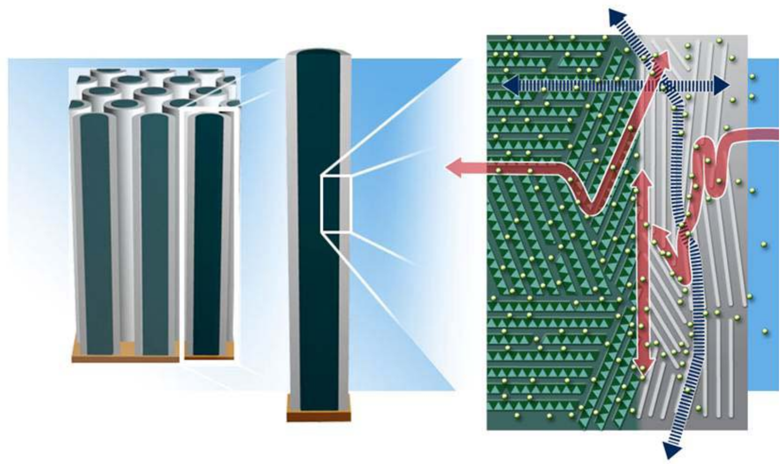
Nanostructures for Electrical Energy Storage (NEES)

EFRC Director: Gary Rubloff

Lead Institution: University of Maryland

Mission Statement: The Center for Science of Precision Multifunctional Nanostructures for Electrical Energy Storage will uncover nanoscale science providing the underpinnings for energy storage technology with dramatically higher power (10-100X) and energy density (10X).

The NEES Energy Frontier Research Center investigates heterogeneous, multifunctional nanostructures as rich platforms for discovering the nanoscale science critical for the next generation of batteries and supercapacitors. Electrode materials in lithium-ion batteries have electrochemical demands for facile, repeatable, and bidirectional transport of ions and electrons and mechanical demands to accommodate large ion densities that cycle in and out repeatedly. The Center's vision holds that heterogeneous combinations of oxides, silicon, and novel forms of carbon in nanostructures promise to meet the multifunctional requirements of electrodes in these storage devices. The Center specifically examines nanostructures that are *precise* – composed of well-defined and closely controlled materials and geometries. This orientation sets a unique course of discovery in kinetics, structural dynamics, and thermodynamics at the nanoscale.



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

The EFRC has four thrust areas. The two Science Thrusts explore the underlying processes that influence and control the behavior of nanostructured electrodes of carbon combined with either an oxide material or silicon. Low dimensional forms of carbon – nanotubes, nanowires, and graphene – in pristine form are both mechanically strong and excellent electronic conductors, while nanoscale oxides and silicon show promise for storing and releasing very high densities of lithium ions at high rates. Combining the expertise of electrochemists, materials scientists, physicists and more, the science thrusts analyze fundamental issues in nanostructure synthesis, charge transport kinetics and structural stability during cycling.

Two Enabling Thrusts support the Science Thrusts by developing models of nanostructured systems and instruments to probe their properties. With experiments and computation, they create models of surface and interface evolution, critical for teasing out the core factors at play in the junctions of heterogeneous structures. The thrusts 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 measure nanostructural changes. Microsystems for in-situ electrochemical TEM are being developed as a Discovery Platform at the Center for Integrated Nanotechnologies, a joint venture between Sandia National Laboratories and Los Alamos National Laboratory, and thus will be available to a wide audience.

The development of new nanoscale characterization methods is enhanced by NEES's priority on precision, regularly ordered nanostructures. Regular testbeds of nanostructures will allow for highly precise and repeatable measurements of nanoscale electrochemistry. The emphasis on order will ultimately be important for successful approaches to synthesizing massive parallel arrays of nanostructured electrodes as needed for next-generation electrical energy storage technology.

Nanostructures for Electrical Energy Storage (NEES)	
University of Maryland, College Park, MD	G.W. Rubloff (Director), S.B. Lee, M.S. Fuhrer, J. Cumings, R. Ghodssi, J. Reutt-Robey, C.S. Wang, Y.H. Wang
Sandia National Laboratories, Albuquerque, NM	S. Hearne, J.P. Sullivan, K. Zavadil, K. Leung
University of California-Irvine	R.M. Penner, P.G. Collins, Zuzanna Siwy
Los Alamos National Laboratory	S.T. Picraux
University of Florida	C.R. Martin
Yale University	M.A. Reed

Contact:

Gary W. Rubloff Minta Martin Professor of Engineering Director, NEES EFRC & Maryland NanoCenter rubloff@umd.edu (301) 405-3011 www.efrc.umd.edu	Ashley Predith Associate Director for Programs NEES EFRC - University of Maryland apredith@umd.edu (301) 405-7801 www.efrc.umd.edu

Center for Excitonics (CE)
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* materials 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).

Our efforts are divided into four working groups, each containing between three and five faculty devoted to key scientific problems confronting the development of more efficient solar cells and solid state lighting.

(i) Coherent exciton dynamics

The aim of this working group is to understand and control coherence in excitonic antennas and exciton polaritons – coherent combinations of excitons and photons. Key topics in this group are our recently developed technique of fully phase coherent 2-d Fourier transform spectroscopy, photosynthetic antennas, and J-aggregates.

(ii) Incoherent exciton dynamics in semiconductor nanocrystals

Here, we seek to understand exciton dynamics in semiconductor nanocrystals using multiexciton spectroscopy and photonic interrogation of single quantum dots in the visible and infrared. Key topics in this group are superconducting nanowire single photon detectors for single dot spectroscopy in the infrared, and extreme nanolithography for managing the interaction between individual semiconductor nanocrystals and photons.

(iii) Solar Antennas

This working group seeks to use excitonics to collect, concentrate, and wavelength-convert sunlight for single junction solar cells, thereby increasing their efficiencies beyond conventional limits (>30%). Key topics for this team are: singlet exciton fission and solar-powered lasers for coherent upconversion.

(iv) Solid State Lighting

This group is developing materials and concepts for reliable and efficient solid state light sources. Key research topics are III-V nanowires, all-inorganic LEDs, the interaction of excitons and charges, characterization of structure-function relationships using Cathodo-Luminescence Scanning Transmission Electron Microscopy (CL-STEM), and the impact of stress on luminescence.

Center for Excitonics	
Massachusetts Institute of Technology	M.A. Baldo (Director), A. Alexander-Katz, M.G. Bawendi, K.K. Berggren, V. Bulovic, J. Cao, M. Dinca, S. Gradecak, J. Moodera, K.A. Nelson, B. Olsen, T.M. Swager, H. Tuller, T. Van Voorhis
Harvard University	A. Aspuru-Guzik, K. Crozier, M. Loncar
Brookhaven National Laboratory	C. Black, E. Stach

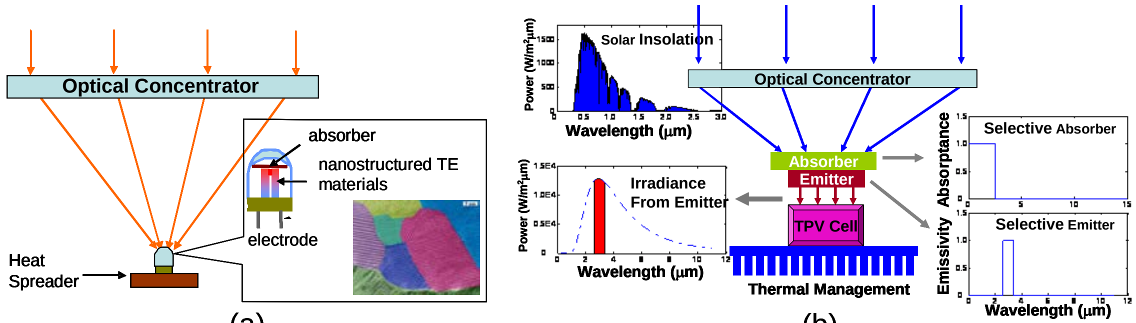
Contact: Marc Baldo
baldo@mit.edu
617-452-5132
http://www.rle.mit.edu/excitonics/

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. 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 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,



(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.

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.

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, S.-G. Kim, Y. Lee, 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
Rensselaer Polytechnic Institute (seed funding)	T. Borca-Tasciuc and G. Ramanath

Contact: Gang Chen
Carl Richard Soderberg Professor of Power Engineering
gchen2@mit.edu
617-253-0006
http://s3tec.mit.edu/

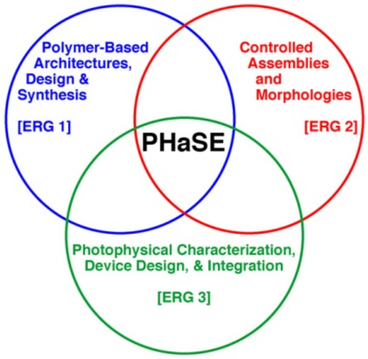
Polymer-Based Materials for Harvesting Solar Energy (PHaSE)

Thomas P. Russell and Paul M. Lahti, Co-Directors
University of Massachusetts Amherst

Mission Statement: The goal of the EFRC led by the University of Massachusetts Amherst is to carry out fundamental photovoltaic-oriented research using organic-based polymers and related materials to maximize efficiency in the collection and harvesting of energy over a broad frequency range of the solar spectrum. The center's strongly-networked, interdisciplinary teams of researchers seek ways to minimize charge-quenching exciton recombination, to maximize electron transport across inorganic/organic interfaces, and to optimize design and fabrication strategies for making inexpensive photovoltaic devices.

Center Research Portfolio:

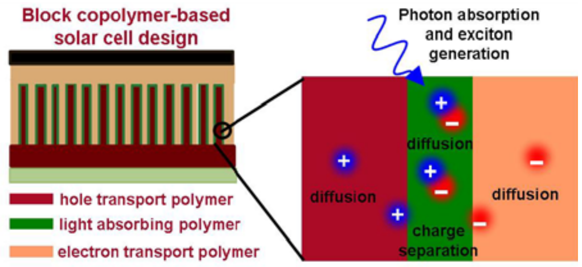
The University of Massachusetts EFRC integrates investigators from multiple departments and institutions into three distinct but cooperating Energy Research Groups or ERGs: ERG 1 *Polymer Based Architecture: Design and Synthesis*, ERG 2 *Controlled Assemblies and Morphologies*, ERG 3 *Photophysical Characterization, Device Design and Integration*. Synthetic work in ERG 1 is complemented by collaborations with the Global Research Laboratory at Seoul National University, the University of Bayreuth and the Heeger Institute at the Gwangju Institute of Science and Technology. Morphological studies in ERG 2 are augmented by theoretical studies of hierarchical ordering with the University of Pittsburgh, and by theoretical studies of exciton dissociation at organic-organic and organic-inorganic interfaces with the Oak Ridge National Laboratories and with Rensselaer Polytechnic Institute. Physico-chemical and test-device work in ERG 3 is augmented by collaborations at the University of Massachusetts Lowell and Konarka. Preparation of anatase titania nanorods and nanotubes is done at The Pennsylvania State University. Inorganic nanoparticle/nanorod synthesis and assembly is pursued at the World Premier Institute, Advanced Institute of Materials Research at Tohoku University. In appropriate cases, the efficiencies of test devices produced by this EFRC will be evaluated and benchmarked at the National Renewable Energy Laboratory.



ERG 1. 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. Most of these targets are designed for light harvesting and photocurrent generation, for integration into the active layers of photovoltaic (PV) devices. Synthetic strategies focus on molecular self-assembly for morphological control, plus processibility of polymer and molecular species with structure-tunable photophysical characteristics that can aid more efficient PV behavior. A unifying objective of all work is to provide a range of polymer and nanocomposite materials for morphological and PV device studies undertaken in ERGs 2 and 3.

ERG 2. The design and fabrication of a high-efficiency PV device requires precise control over the nanoscale morphology, molecular ordering, and interfacial properties of all components comprising the device. While easy to state, these tasks are practically challenging; most research on polymer-based PV devices to date typically studies just one such task in detail. ERG 2 integrates researchers with well-established expertise in synthesis, as well as theory and engineering of polymers to control self-assembly of polymers and to manipulate polymer morphologies and individual chains in thin films. This expertise will be used to develop routes to control morphology and structure of polymer-based and polymer/inorganic-based hybrid materials so as to optimize photovoltaic efficiency. The knowledge gained from these studies can then be used in device-fabrication strategies.

ERG 3. In an organic solar cell, the conversion of light energy to electric current involves several fundamental processes: (1) absorption of light to create excitons, (2) diffusion of excitons to a region of high electric potential mismatch where charge separation can occur, (3) charge separation, (4) charge transport of holes and electrons to their respective electrodes, and (5) transport of the carriers across the respective organic-electrode interfaces (see figure to right). All of these processes need to be understood to optimize them for higher efficiency solar cells. Detrimental effects – like charge carrier recombination and trapping – need to be assessed to identify structures that inhibit these effects. By state-of-the-art time-resolved optical techniques it is possible to distinguish and quantify the lifetimes and evolution mechanisms of these processes.



Various processes ongoing in a generic organic-based photovoltaic cell.

A primary goal of ERG 3 is to elucidate photophysical details of charge and energy transport within nanostructured photovoltaic composite films. Single-molecule and time-resolved spectroscopies provide valuable mechanistic insight about the behavior of the synthetic building blocks and their molecular architecture on the primary processes in PV systems. The "feedback loop" of design * synthesis-assembly * physical process evaluation * test device evaluation and back again allows identification of the most promising strategies for more rigorous PV device fabrication and testing in collaboration with UMass Lowell and industrial collaborator Konarka Technologies Inc.

Polymer-Based Materials for Harvesting Solar Energy (Lead Personnel)	
University of Massachusetts Amherst	*Directors*: T. P. Russell, P. M. Lahti *Senior Personnel* (*ERG Coordinators*): M. D. Barnes, T. S. Emrick, D. Venkataraman; *Senior Personnel*: A. Briseno, K. Carter, E. B. Coughlin, A. Crosby, A. Dinsmore, G. Grason, R. Hayward, D. Maroudas, V. Rotello, S. Thayumanavan, C. Santangelo, J. Watkins
University of Pittsburgh	*Senior Personnel* (*subcontract site lead investigator*): A. C. Balazs
The Pennsylvania State University	*Senior Personnel* (*subcontract site lead investigator*): T. Mallouk
University of Massachusetts Lowell	*Senior Personnel* (*subcontract site lead investigator):* J. Kumar
Oak Ridge National Laboratory	*Senior Personnel* (*major collaborator*): B. Sumpter
Rensselaer Polytechnic Institute	*Senior Personnel* (*major collaborator*): V. Meunier

Contact:

Professor Thomas P. Russell
Polymer Science and Engineering
russell@mail.pse.umass.edu
413-577-1516

Professor Paul M. Lahti
Chemistry
lahti@chem.umass.edu
413-545-4890

http://www.cns.umass.edu/efrc

Center for Solar and Thermal Energy Conversion (CSTEC)
EFRC Director: Peter F. Green
University of Michigan, Ann Arbor, MI

Mission Statement: Researchers in CSTEC investigate fundamental processes that govern the efficiency of solar and thermal energy conversion in nanostructured, complex, and low-dimensional inorganic, hybrid, and organic materials.

The efforts of the center are organized into three main areas: (1) the ***Inorganic PV*** thrust investigates site-controlled nanostructures, Type-II band-offset materials, and highly mismatched alloys; (2) the ***Thermoelectric*** thrust studies the properties of single-molecular junctions, quantum-dot structures, thin films, and bulk nanocomposites; and (3) the ***Organic and Hybrid PV Materials*** thrust investigates (a) absorption phenomena in organic and hybrid systems and (b) molecular design, carrier transport and device performance.

1. Inorganic PV Thrust: Though the highest efficiency PVs are based on inorganic materials, further increases in efficiency will require mitigating intrinsic loss processes. Thus, the inorganic PV thrust aims to identify and to develop materials with exceptional electronic transport properties capable of absorbing energy efficiently from a broader range of the solar spectrum. The focus is to understand the relationships between interface structure, photo-absorption, and carrier transport in low-dimensional and nanostructured materials. Of particular interest are systems that show promise for intermediate band solar energy conversion, including site-controlled nanostructures, staggered Type-II band-offset materials, and highly mismatched alloys. Specific systems under investigation include InAs/GaAs and InGaN/GaN site-controlled quantum dots; ZnTe/ZnSe, GaSb/GaAs, and GaAsB/GaAsBi staggered Type-II band-offset materials; and highly mismatched alloys including ZnTe/ZnSe, GaSb/GaAs and GaAsN/GaAsBi. The schematic in Figure 1 summarizes our overall strategy.

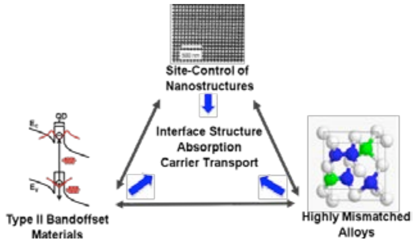


Figure 1: Overview of inorganic PV research

2. The Thermoelectric Thrust of CSTEC focuses on theoretical and experimental investigations of fundamental mechanisms governing carrier transport processes and energy conversion efficiency in low-dimensional (single-molecular junctions, quantum-dot structures, and thin films) and a specific class of bulk thermoelectric materials. Experimental efforts include: (a) synthesis of novel TE materials using equilibrium and far-from-equilibrium molecular beam epitaxy (MBE) growth processes, (b) the development of new and highly sensitive methods of thermal property and carrier transport measurements at the nanoscale, and (c) unique ultrafast optical studies of carrier and phonon dynamics (Fig. 2). Experimental work is complemented by *ab initio* approaches and cluster expansion methods used to calculate phase diagrams as well as molecular dynamics simulations of phonon conductivity (heat transport).

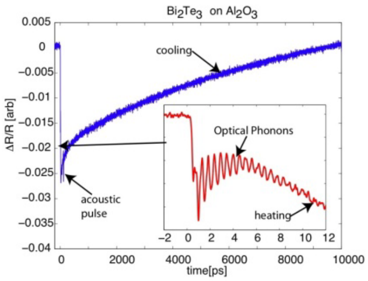


Figure 2: Ultrafast spectroscopy measurement of phonon dynamics

Current research problems include: (a) understanding electronic and phonon transfer at metal-organic molecule-metal junctions (MMMJ), (b) modifying carrier and phonon dynamics through judicious manipulation of structure in thin films and nanostructured materials, and (c) investigating structural order-disorder transitions and phonon conductivity of partially filled skutterudites using combined experimental and theoretical methods in order to improve the thermoelectric figure-of-merit.

3. Organic and Hybrid PV Thrust: The chemical structure and long and short-range molecular organization of organic semiconductors strongly influence their absorption properties and mechanisms of charge generation, transport, and separation. To understand and improve these processes, the thrust is organized into two main areas: (a) absorption phenomena and (b) molecular design, nanoscale characterization, and device efficiency.

(a) The absorption effort focuses on understanding and maximizing absorption while mitigating energy losses in caged systems, nanotubes, and self-aligning polythiophene derivative based organic polymers. The specific strategies investigated leverage the enhancement of absorption due to intra-molecular interactions and plasmonic effects associated with metal particles dispersed in small molecular and polymeric organic films. Molecular dynamics simulations and DFT calculations are being used to investigate the electronic structure, excitation dynamics, charge and energy transport in caged compounds.

(b) Researchers in the molecular design, nanoscale characterization, and device efficiency effort are involved with materials synthesis (caged systems, self-aligning polythiophene derivative based organic polymers, small molecule organic/C_{60} systems) with the goal of understanding and improving charge transport at different length scales. Of particular interest are charge transfer processes at interfaces in organic and hybrid PV systems. Here too, computational molecular design efforts are used to predict material properties and guide experimental synthesis.

CENTER FOR SOLAR AND THERMAL ENERGY CONVERSION (CSTEC)	
University of Michigan, Ann Arbor	Peter Green (Director), Rachel Goldman (Assoc. Director) , Ctirad Uher (Assoc. Director), Roy Clarke, Barry Dunietz, Steve Forrest, Theodore Goodson III, John Kieffer, Jinsang Kim, P.C. Ku, Ted Norris, Xiaoqing Pan, Kevin Pipe, Max Shtein, Eitan Geva, 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, Director
Pfgreen@umich.edu
www.cstec.engin.umich.edu

Revolutionary Materials for Solid State Energy Conversion (RMSSEC)
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); an example is the Auger mapping capability illustrated in **Figure 2**.

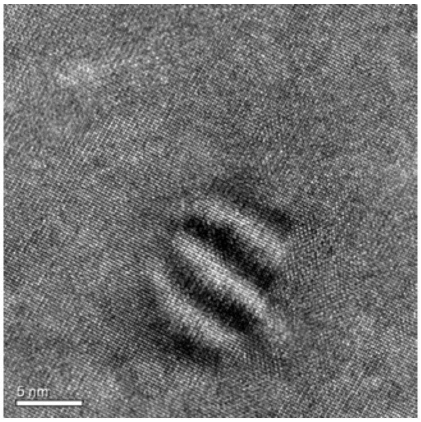


Figure 1 High resolution TEM image showing spinodally decomposed regions in PbTe-16%PbS.

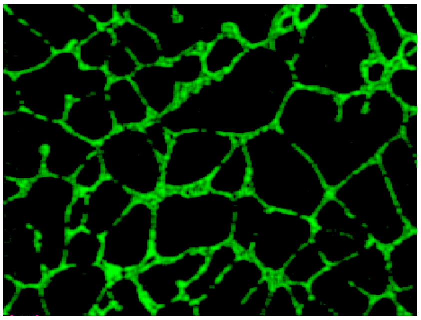


Figure 2 Auger map of boron (green) decorating grain boundaries in a Co-Si alloy.

Center for 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	E. Lara-Curzio
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, Professor of Materials Science
Michigan State University
dmorelli@egr.msu.edu
www.egr.msu.edu/efrc/

Center for Inverse Design (CID)
EFRC Director: Bill Tumas
Lead Institution: National Renewable Energy Laboratory

Mission Statement: *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, developing new materials for technological applications has largely been based on trial-and-error searches or accidental discoveries. However, this practice may not be the best way to find game-changing technologies because: (i) in many cases, materials with fundamentally new properties are outside the chemical neighborhood of the "usual suspects" materials, and (ii) developing accidentally discovered materials may take a long time (since it takes a long time to determine what it is that has been discovered).

We prefer, in principle, *materials design* over materials discovery. Our center's revolutionary research uses quantum theory and high-performance computers to design new materials having desired properties. Then we use state-of-the-art high-throughput synthesis and targeted synthesis to converge on those materials in the laboratory.

Figure 1 shows that our approach resembles "Quantum Jeopardy": Given the answer (e.g., a certain unique and useful material property), find the question (e.g., what material is it?). Stated another way, traditional accidental discovery says: "Give us the structure; we'll study its properties," whereas our center's approach reverses this norm to: "If these are the properties we want, we'll find the structure."

Fig. 2. Inverse-design approach versus conventional (materials discovery) approach.

The vision of Inverse Materials Design could change the basic approach to materials research and potentially usher in a new era of materials science. The methodology combines and integrates theory (prediction), synthesis (realization), and characterization (validation). Its successful implementation will accelerate by orders of magnitude the development of new materials. The four steps that we are following are described below.

First, we articulate a set of desired, physical target properties. For *optoelectronic materials*, including solar semiconductors and insulators, the target properties might include achieving the following: a direct-bandgap system out of indirect-gap constituents (such as Si and Ge); a given positioning of band-edge energies with respect to certain redox potentials; a target anisotropy of the effective masses conducive to conductivity or thermoelectricity; or the ability to dope a material *p*-type or *n*-type. For *ferromagnets*, the target might be a desired Curie temperature. For *impurities in solids*, a target might be a certain energetic position of the impurity (donor or acceptor) levels with respect to the band edges. For *topological insulators*, a target might be to invert the order of conduction and valence bands; and for *quantum wires and dots*, a target might be a certain Auger recombination, spin-splitting, or exciton-multiplication rate.

Second, for given target properties, we select an initial set of *broad material class*—based on "design principles" distilled from past insights and calculations—likely to encompass the required target properties. For new solar absorbers and transparent conducting oxides, we have selected ternary chalcogenides and pnictides, including hundreds of candidate materials that are simply missing from standard material compilations. We ask: Are they missing for a good reason (e.g., they are intrinsically unstable), or have they simply been overlooked and could potentially be game-changing materials?

Third, we identify—via theoretical searching of the above-noted material and structure spaces—the sub-class whose electronic properties are close to the target property. The search-space might include either (i) *configurational degrees of freedom* at fixed composition (such as lattice decoration by Si and Ge atoms leading to direct gap), or (ii) *shape degrees of freedom* of quantum dots/wires leading to given spectroscopic property, or (iii) *compositional degrees of freedom* (different elements constituting a compound). We use high-throughput electronic structure, defect and nanostructure calculations, and genetic or other biologically inspired search algorithms in conjunction with quantum-mechanical calculations. For example, we have performed such calculations for hundreds of A_2BX_4 and A_3BX_4 chalcogenides and ABX "filled tetrahedral structures." This work has uncovered previously unsuspected but stable "missing compounds," as well as fundamental "doping rules" that control carrier introduction into wide-gap oxides, rendering them "transparent conducting oxides."

Fourth, we study the candidate structures and materials narrowed down from an initial astronomical number to a more manageable range. We use both combinatorial synthesis and targeted synthesis, followed by material characterization. The latter steps involve an *iterative process* between experiment and theory—where 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—eventually converging on the target.

We believe our approach applies to a broad range of material properties (e.g., topological insulators, magnetism, ferroelectricity, superconductivity, transparent conductors) and structures (e.g., solids, alloys, nanostructures, molecular structures). Our center is generating general methodologies to be tested on specific cases, but having future potential to open the door for much broader applications.

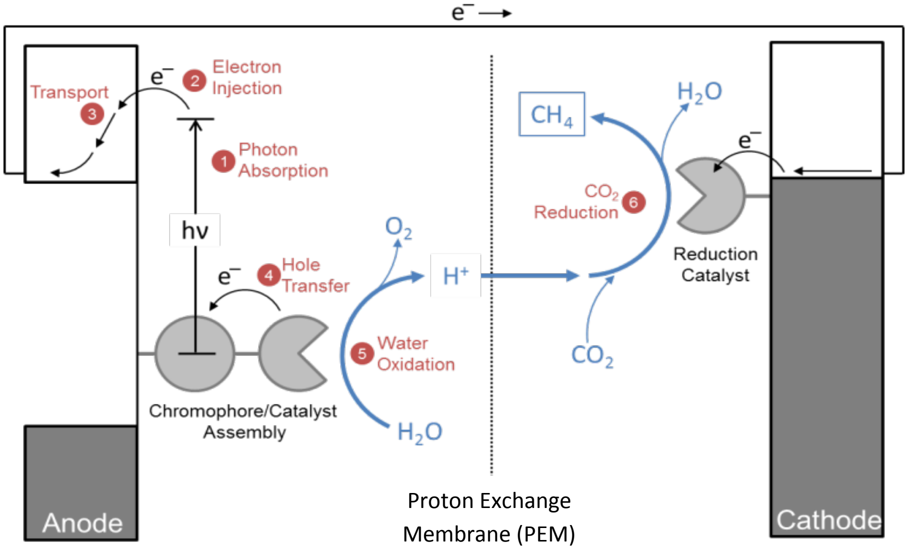
Center for Inverse Design	
National Renewable Energy Laboratory (lead institution)	B. Tumas (Director), L.L. Kazmerski, D.S. Ginley, J.D. Perkins, S. Lany, M. d'Avezac, P.A. Graf, J.W. Luo
University of Colorado	A. Zunger, L. Yu
Colorado School of Mines	V. Stevanovic
Northwestern University	A.J. Freeman, K.R. Poeppelmeier, T.O. Mason
Oregon State University	J.F. Wager, D.A. Keszler
SLAC / Stanford University / SSRL	M.F. Toney

Contact: Bill Tumas, (Director); Bill.Tumas@nrel.gov, http://centerforinversedesign.org/

Center for Solar Fuels (UNC)
EFRC Director: Thomas J. Meyer
Lead Institution: University of North Carolina at Chapel Hill

Mission Statement: We will combine 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.

The UNC EFRC is conducting research on capturing sunlight to drive solar fuel reactions. The Center's efforts range from basic research on fundamental processes to integrating components into sub-systems and sub-systems into prototypical devices. The research utilizes a broad, multidisciplinary approach in a highly collaborative setting drawing on expertise across a broad range of disciplines in chemistry, physics, and materials sciences. The primary target is a Dye Sensitized Photoelectrosynthesis Cells (DSPEC) for solar fuels production as illustrated below.



Dye-Sensitized Photoelectrosynthesis Cell (DSPEC)

SOLAR FUELS

Multiple platforms are under investigation but the primary focus is on Dye Sensitized Photoelectrosynthesis Cells (DSPEC). This approach utilizes molecules and molecular assemblies for catalysis in photoelectrochemical configurations closely related to those used in Dye Sensitized Solar Cells (DSSC). The Figure shows a schematic diagram for a DSPEC for light driven water reduction of CO_2 to methane. In contrast to a DSSC, where the target is creating a photopotential and photocurrent, the target of a DSPEC is production of a high energy fuel with oxygen as the co-product in the physically separated compartments of a photoelectrochemical cell. **The UNC EFRC focus is on a modular approach which entails constructing and maximizing component performance, as well as integration into device prototypes featuring both single and tandem light absorption.**

The focus first has been on separate functions for solar fuels formation ‑ light absorption, excited state electron and energy transfer, electron and proton transfer driven by free energy gradients, and catalysis of water oxidation and water/CO_2 reduction ‑ all integrated in a photoelectrochemical cell configuration. In the modular approach the separate components are designed and tested for maximum performance and then integrated into the final DSPEC architecture. DSPEC research benefits and is enriched by parallel research in electrocatalysis, Dye Sensitized Solar Cells, and Organic Photovoltaics.

Hallmarks of Center research are: (1) fundamental studies on reaction mechanisms, (2) synthesis of novel materials combining light absorption and catalysis, (3) preparation and characterization of designed photocatalytic interfaces, (4) application of theory and experiment to guiding principles for component design, integrated systems, and devices, and (5) augmentation of research findings and multidisciplinary strengths in collaborations with national laboratories, other EFRCs, and the Research Triangle Solar Fuels Institute (www.solarfuels.org).

TEAM STRUCTURE and RESEARCH FOCUS

The Center employs an integrated, interdisciplinary team-based approach in Solar Fuels based on four research areas, **Catalysis**, **Assemblies, Interfacial Synthesis and Characterization**, **Device Prototypes.** Ten research teams, led by faculty members at UNC and partner institutions, pursue research in these areas.

RESEARCH THRUST	TEAM	TEAM RESEARCH FOCUS
Catalysis	Water Oxidation	Development of new solution and interfacial catalysts for water oxidation.
	CO_2 Reduction	Development of new solution and interfacial catalysts for CO_2 reduction.
Assemblies	Polymers	Synthesis and characterization of molecular assemblies based on polymer scaffolds for multi-chromophore applications.
	Peptides	Molecular assemblies based on peptide scaffolds for control of chromophore/catalyst geometry.
	Framework Materials	Organic-inorganic hybrid materials for integrated light-harvesting and catalysis.
Interfacial Synthesis and Characterization	Interface Synthesis	Synthesis and attachment of chromophore-catalyst assemblies at metal oxide interfaces.
	Interface Characterization	Characterization of interfacial structure and dynamics by transient and surface spectroscopies.
Device Prototypes	DSSC/DSPEC Devices	Evaluation and performance of integrated catalysts, assemblies and new transparent metal oxide semiconductors in device prototype configurations.
	Organic Photovoltaic Devices OPV	Fabrication and characterization of devices with new approaches to 3-D charge collection.
Theory	Theory	Research integrated across the Center on reaction pathways, electron and energy transport, molecular design, systems analysis

CENTER FOR SOLAR FUELS	
University of North Carolina at Chapel Hill	T.J. Meyer (Director), K. Brennaman, M. Brookhart, J. Concepcion, C. Fecko, M. Forbes, Y. Kanai, S. Keinan, W. Lin, S. Liu, R. Lopez, A. Moran, R. Murray, J. Papanikolas, L-C. Qin, E. Samulski, C. Schauer, J. Templeton, M. Waters, Y. Wu, W. You
Duke University	D. Beratan, M. Therien, W. Yang
Georgia Institute of Technology	J. Reynolds
North Carolina State University	P. Maggard
North Carolina Central University	D. Taylor
University of Florida	K. Schanze
University of Maryland	G. Papoian
Research Triangle Institute	P. Hoertz

Contact: Thomas J. Meyer , Arey Distinguished Professor of Chemistry
tjmeyer@unc.edu, www.efrc.unc.edu

* Updated February 2012

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 explores 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 is built around a core (a “Think Tank”) of expert theorists that interact closely with experimentalists working in four carefully selected “Focus Areas” combining the fundamentals of non-equilibrium research with the practice and applications of energy-related material systems, namely *Plasmoelectronics*, *Mechanochemistry*, *Chemical Networks*, and *Fundamental Theory of Dissipative Systems*. Each and every project we pursue combines experiment with theory. The underlying motive is that experimental effort without any quantitative or theoretical component can rapidly deteriorate into a quest for specific molecules/structures; theory without experiment can lead to practically irrelevant models and/or theories. Instead, our vision is to establish a general methodology for the rational design of adaptive, non-equilibrium materials. Second, we pursue a bottom-up approach, in which non-equilibrium, adaptive systems and materials are built (or self-assembled) from simple components. The bottom-up approach enables us to test theoretical hypotheses at increasing levels of system complexity.

We focus on hard, soft, and hybrid materials. Theory, modeling and simulation efforts, fully integrated with synthesis and characterization, 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 (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 material systems exhibit at least two characteristics that make them relevant to energy-related applications: (i) Their adaptability to the energetic "status" of the environment can translate into the ability to harness "waste" energy from the environment. (ii) Because non-equilibrium ensembles necessarily entail spatial thermodynamic gradients, they can direct and/or transduce this energy into useful work.

In systems displaced from thermodynamic equilibrium – either into kinetically trapped states or into states, the production of entropy (i.e., dissipation of useful energy) directs the emergence of order. Although virtually all animate systems fall into one of these categories, our knowledge of the non-equilibrium regime is painfully inadequate and the identification of general and predictive rules that describe systems far-from-equilibrium remains one of the greatest challenges of modern science. Despite its difficulty, this challenge is certainly worth undertaking – not only for its fundamental appeal but also for the practical promise. Because they can reside in multiple steady-states controlled by the flux of externally delivered energy (chemical, electromagnetic, or thermal), non-equilibrium systems can adapt to changing environmental conditions, adjust the mode of internal organization, and perform different functions depending on the state of experimental signals/controls. Creation of such "adaptive" systems and materials that maintain themselves away from thermodynamic equilibrium require multifunctional and adaptive building blocks. Changing the properties of such blocks by external inputs/stimuli can then lead to changes in material's structure and/or function (Figure 1).

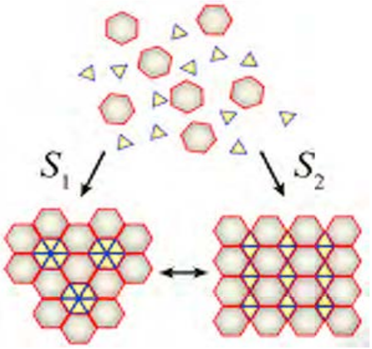


Figure 1. Different stimuli, *S*, evolve the same set of components into different "adaptive" materials.

A cornucopia of creative examples of non-equilibrium systems exist in Nature, many of which are related to energy harnessing (photosynthesis), transport (proticity), or transduction (motor proteins). Our Center's goal is to learn how to use the non-equilibrium phenomena as skillfully and efficiently as Nature does, by thinking about new synthetic systems and supporting this effort by theoretical input and foundation.

Non-equilibrium Energy Research Center (NERC)	
Northwestern University	B.A. Grzybowski (Director), I. Szleifer (Associate Director), C. Mirkin, M.O. de la Cruz, M.A. Ratner, G.C. Schatz, J.F. Stoddart, S.I. Stupp, E. Weiss
Harvard University	G.M. Whitesides
University of Michigan	S.C. Glotzer
The Pennsylvania State University	K.J.M. Bishop

Contact: Bartosz A. Grzybowski
Professor of Physical Chemistry and Chemical Systems' Engineering
nerc@northwestern.edu
847.467.1295 (Ms. Leah Seiffert, Program Assistant)
www.nercenergy.com

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

Mission Statement: 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 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
- energy levels and electronic structures of molecules and materials
- dynamics of photoinduced charge generation, separation, and transport with unparalleled temporal and spatial resolution
- interfaces at which charge generation, separation, transport, and selective chemical reactions occur
- 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 splitting 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. Subtask 1 research targets discovering the fundamental scientific principles necessary to 1) self-assemble biomimetic molecular systems to harvest light and perform photochemical charge separation, 2) couple photogenerated charges to multi-electron, multi-metallic catalysts for H_2O oxidation and H^+ reduction to H_2, and 3) develop bio-inspired supramolecular assemblies to produce tailored nano-environments necessary for an integrated artificial photosynthetic system (e.g. Fig. 1).

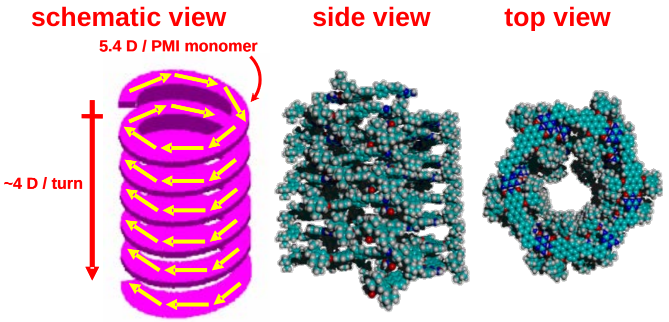


Fig. 1. Self-assembling nano-environment for integrated artificial photosynthesis.

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. Subtask 2 research is directed toward achieving the fundamental understanding required to achieve power conversion efficiencies as high as 10-15%. Progress requires 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 are also exploited in the other types of interfaces necessary to implement the photodriven catalysts and solar cells in Subtasks 1 and 3, respectively.

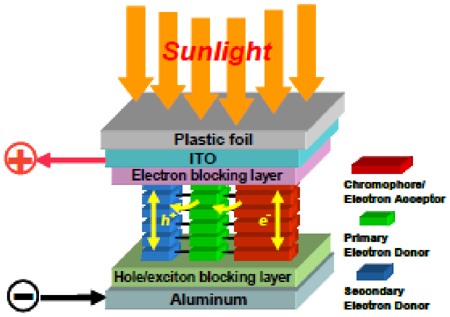


Fig. 2. A multilayer organic solar cell.

Subtask 3: Nanostructured architectures for photovoltaic and photochemical energy conversion. This subtask defines, develops, models, and tests 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, Subtask 3 focuses 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 builds on many of the activities in Subtasks 1 and 2 and synergistically provides information back to these subtasks. DSSCs represent one of the most promising alternatives to expensive silicon technology for conversion of solar radiation to electricity (Fig. 3a). Specifically, we are using 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 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).

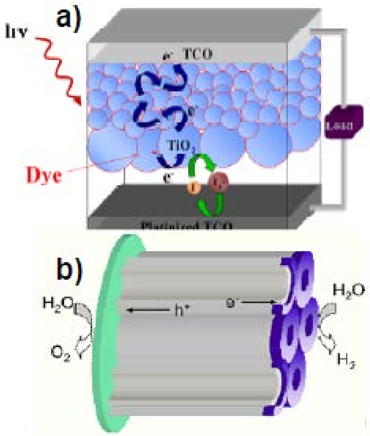


Fig. 3. a) DSSC based on electron injection into a wide bandgap, nanocrystalline, n-type semiconductor. **b)** *Compartmentalized* light-harvesting, catalytic oxidation, and catalytic reduction components function on a high-area, high-porosity, electrically conductive platform.

Argonne-Northwestern Solar Energy Research (ANSER) Center	
Northwestern University	M. R. Wasielewski (Director), R. P. H. Chang, A. Freeman, M. Hersam, J. T. Hupp, M. Kanatzidis, T. J. Marks, T. O. Mason, T. W. Odom, K. R. Poeppelmeier, M. A. Ratner, G. C. Schatz, S. I. Stupp
Argonne National Laboratory	L. X. Chen, J. Elam, A. Martinson, M. J. Pellin, O. Poleuktov, D. Tiede, G. Wiederrecht
Yale University	V. Batista, G. Brudvig, R. Crabtree
Univ. of Illinois, Urbana-Champaign	T. Rauchfuss
University of Chicago	L. Yu

Contact: Michael R. Wasielewski, Director, ANSER Center; m-wasielewski@northwestern.edu
www.ANSERCenter.org

Materials Science of Actinides (MSA)

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 six 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.

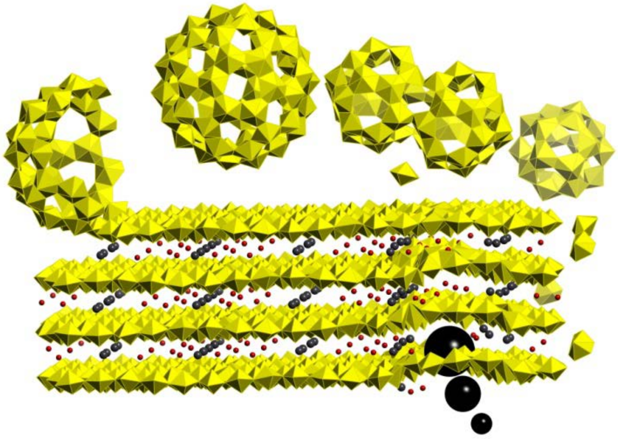
Three major Research Themes in actinide materials science are central to MSA's efforts. These themes are: Complex actinide materials, Nanoscale actinide materials, and Actinide materials under extreme environments. Four cross-cutting themes are: Actinide behavior at the nanoscale, Thermochemistry of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



Understanding complex actinide materials, uranyl peroxide clusters, and materials under extreme environments through synthesis, modeling, thermodynamics, and behavior at the nanoscale.

Materials Science of Actinides	
University of Notre Dame	P.C. Burns (Director), T. Albrecht-Schmitt, J.B. Fein, E. Maginn
University of Michigan	R.C. Ewing, U. Becker, M. Lang
University of California-Davis	A. Navrotsky, W. Casey, M. Asta
George Washington University	C. Cahill
University of Minnesota	L. Gagliardi
Rensselaer Polytechnic Institute	J. Lian
Oak Ridge National Laboratory	W. Weber
Savannah River National Laboratory	D. Hobbs, A. Visser, T. Rudisill
Sandia National Laboratory	M. Nyman

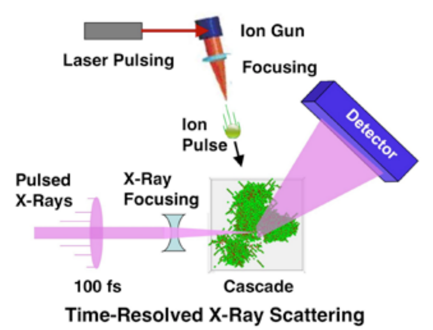
Contact: Peter C. Burns
Director
pburns@nd.edu
574-631-5380
www.ndefrc.com

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.

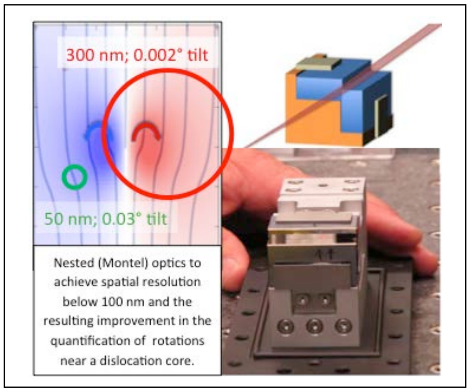
The *Energy Frontier Center for Defect Physics in Structural Materials (CDP),* focuses on providing the fundamental knowledge to allow atomistic control and manipulation of the defects that limit the performance and lifetime of materials. Our goal is to bring a new level of rigor and insight to the study of defect structure, interactions, and dynamics in metals and alloys through quantitative experimental studies of unit events coupled with highly accurate calculations and simulations based on a quantum description of the underlying electronic interactions. Underpinning the CDP is the realization that this new era of *quantitative measurement and simulation* 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 PFlop/s computing power available at the National Center for Computational Science (NCCS) and the National Energy Research Scientific Computing Center (NERSC). The Center focuses on three interrelated research thrust (RT) areas:

RT1: *Fundamental Physics of Defect Formation and Evolution during Irradiation*: Research in this thrust addresses one of the most fundamental and challenging issues in radiation damage – displacement cascades, the sub-picosecond dynamics of which have been studied by molecular dynamics (MD) simulations for over 50 years without a single experiment. Here, the underlying science of the formation and evolution of energetic-ion induced atomic displacement cascades as unit events will be probed 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 LCLS x-ray pulses and high brilliance APS beams. Parallel simulations of cascade formation and evolution employing MD and a newly developed object Monte Carlo method will provide a basis for simulating diffuse scattering and interpreting the critical x-ray measurements. Together, the computational and experimental components are directed toward obtaining a full understanding of the generation, accumulation, and the potential for mitigating radiation damage in structural materials.



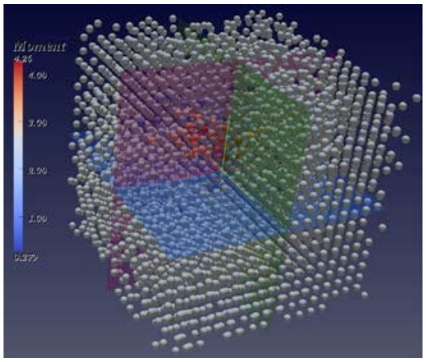
Sub-picosecond to millisecond resolution x-ray diffuse scattering probe of cascade dynamics using the LCLS and the APS.

RT2: *Fundamental Physics of Defect Interactions during Deformation*: Research in this thrust addresses fundamental and longstanding issues associated with achieving a quantitative understanding of the local stresses on single dislocations, their aggregates, and the stress-driven interactions of dislocations with microstructural features (e.g. grain-boundaries). 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 nanoindenter-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. State-of-the-art transmission electron microscopy techniques, including 3D electron tomography, will be used to independently characterize the detailed defect structures present in the analyzed volumes. All measurements will be performed in close synergy with first-principles-based theory and simulations in RT3.



Nested (Montel) optics to achieve spatial resolution below 100 nm and the resulting improvement in the quantification of rotations near a dislocation core.

<u>RT3: *Quantum Theory of Defects and Interactions*:</u> Research in this thrust will overcome limitations of density functional theory (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 new DFT functions will be developed. The leadership computing resources of the NCCS and NERSC facilities will be used to advance the state of the art in classical ion-spin dynamics and diffusive atom density MD through the inclusion of spin degrees of freedom.



Local magnetic moment distribution at t=0.146 ps during a 500eV displacement cascade simulation of radiation damage in a 9826-atom BCC supercell of Fe

Center for Defect Physics (CDP)	
Oak Ridge National Laboratory	G. Malcolm Stocks (Director), Jamie Morris (Deputy Director Administration), Roger Stoller, Easo George, Don Nicholson, Ben Larson, Eliot Specht, Sarma Gorti, Paul Kent, Jeongnim Kim, Yury Osetskiy, Rad Radhakrishnan, German Samolyuk, Jon Tischler, Steve Zinkle
University of Illinois	Ian Robertson
Ohio State University	Mike Mills
Brown University	Sharvan Kumar
Lawrence Livermore National Laboratory	Randy Hood
University of California Berkeley	Andy Minor
Carnegie Mellon University	Yang Wang
University of Tennessee	George Pharr, Yanfei Gao
Ames Laboratory	Duane Johnson

Contact: G. Malcolm Stocks, Director
stocksgm@ornl.gov
(865) 574-5163
http://cdp.ornl.gov

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

Mission Statement: To develop fundamental understanding and validated, predictive models of the unique nanoscale environment at fluid-solid interfaces that will enable transformative advances in electrical energy storage and catalysis for energy.

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 energy and 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 and potential gradients (electrical and/or chemical) to influence chemical reactions, ionic and molecular transport and charge transfer within and across the interface?
- How can we control and predict interfacial phenomena by informed design of fluid- and solid-phase components, interfacial geometries, field gradients and environmental parameters?

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. 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 capacitors), heterogeneous catalysis, and chemical separations. 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.

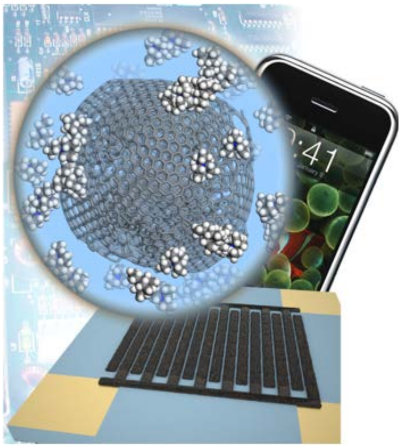


Figure 1. Microsupercapacitors developed with novel carbon nano-onion electrodes exhibit extremely high power density (Pech, Gogotsi, et al., *Nature Nanotechnology* **5**, 641, 2010). We are now investigating the origins of this behavior using X-ray and neutron scattering, electrochemical and molecular modeling approaches.

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 and destruction. To achieve true predictive understanding of such systems, our strategy is hierarchical and highly-integrated, coupling unique experimental, chemical imaging, materials synthesis and computational approaches to probe FSI structures, reactions, and transport phenomena. In Thrust 1, we investigate organic and inorganic electrolyte interactions with charged and uncharged carbon surfaces in a planar or unconfined geometry. This enables coupling of advanced neutron, X-ray, NMR and nonlinear optical probes of interfacial structure and dynamics with multiscale computational models that capture the chemical realism of interfaces. In Thrust 2, we 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 (Figure 1). In Thrust 3, we seek to identify the unique properties of interfacial fluids that control reaction pathways, selectivity, and energetics of proton-coupled electron transfer reactions involving CO_2 and O_2. The goal of these thrusts is to develop predictive FSI models that capture the actual structures, compositions and solute-solvent-substrate interactions that control interfacial properties, reactivity and transport.

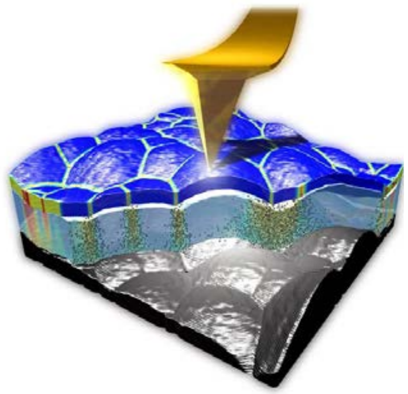


Figure 2. Electrochemical Strain Microscopy, being developed jointly by the FIRST Center and ORNL's user-driven Center for Nanophase Materials Sciences, reveals the diffusional dynamics of lithium ions in working battery electrodes with nanometer resolution (Balke et al, *Nano Letters* **10**, 3420, 2010).

The research is 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 is conducted through peer-reviewed proposals to 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 Center currently supports 20 students and postdoctoral fellows at ORNL and our partner institutions.

Fluid Interface Reactions, Structures and Transport (FIRST) Center	
Oak Ridge National Laboratory	David J. Wesolowski (Director), L.M. Anovitz, N. Balke, G.M. Brown, A.A. Chialvo, S. Dai (Deputy Director), N.J. Dudney, E.W. Hagaman, D. Jiang, P.R. Kent, A.I. Kolesnikov, S. Mahurin, E. Mamontov, K.L. More, S.H. Overbury, G. Rother, R.W. Shaw, R.R. Unocic, Z. Wu
Vanderbilt University	P.T. Cummings
Argonne National Laboratory	P.A. Fenter
Drexel University	Y. Gogotsi, K.L. Shuford
University of Virginia	M. Neurock
Northwestern University	F. M. Geiger

Contact: David J. Wesolowski, Director, FIRST EFRC; wesolowskid@ornl.gov; 1-865-574-6903
http://www.ornl.gov/sci/first/

The Center for Molecular Electrocatalysis (CME)
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 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 addresses fundamental challenges in understanding how molecular electrocatalysts function, and uses this knowledge to rationally design new classes of molecular electrocatalysts for important energy storage and utilization reactions. Closely coupled experimental and theoretical studies include inorganic synthesis, ligand design, mechanistic studies, electrochemical and spectroscopic measurements, determination of thermochemical values for metal hydride complexes, and evaluation of catalytic activity.

Electrocatalytic reactions studied are 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 is 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 in the Center for Molecular Electrocatalysis exhibit activities for hydrogen production comparable to, or exceeding 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.*

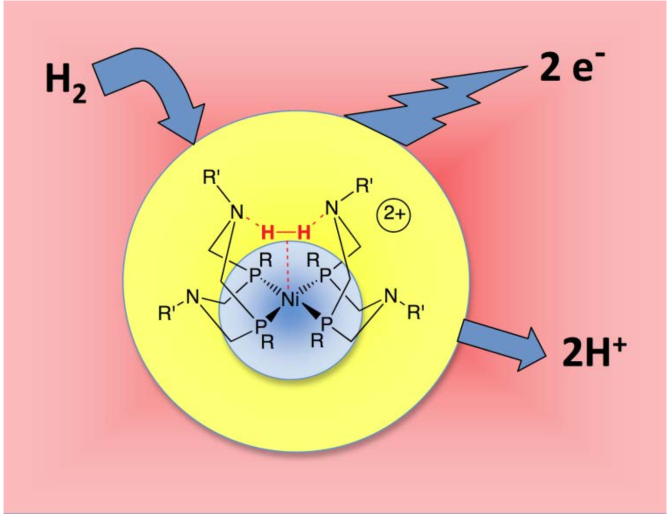
The reduction of protons derived from water to form hydrogen is shown in eq. 1 (forward direction). The reverse process, the oxidation of H_2, is an important reaction in hydrogen fuel cells. The four-electron reduction of O_2 to form water, (eq. 2, forward direction), is important in almost all currently 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. As currently carried out, however, most of the H_2 used in the Haber-Bosch process is produced by steam reforming of methane. Use of protons and electrons instead of H_2 would avoid the use of fossil fuels to produce the H_2.

$$2\,H^+ + 2\,e^- \rightleftharpoons H_2 \tag{1}$$

$$O_2 + 4\,H^+ + 4\,e^- \rightleftharpoons 2\,H_2O \tag{2}$$

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

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 primary 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 multi-proton, multi-electron reactions required for a secure energy future.

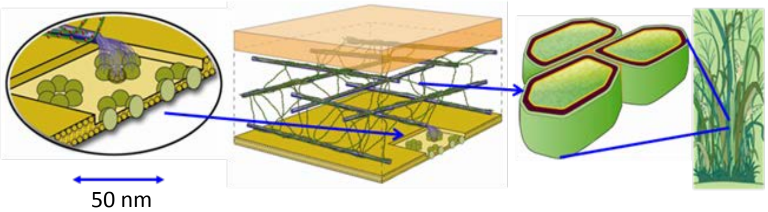
Center for Molecular Electrocatalysis	
Pacific Northwest National Laboratory	R. Morris Bullock (Director), Daniel L. DuBois (Deputy Director), Michel Dupuis, Roger Rousseau, Simone Raugei, John A. S. Roberts, Aaron Appel, John, Linehan, Michael T. Mock, Wendy J. Shaw
University of Washington	James M. Mayer
Pennsylvania State University	Sharon Hammes-Schiffer
University of Wyoming	Bruce A. Parkinson

Contact: Morris Bullock
Laboratory Fellow
morris.bullock@pnl.gov
http://efrc.pnl.gov/

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 the most abundant 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 CLSF, which has 3 interrelated themes, illustrated at right.

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:



Center theme 1: Understand Cellulose synthesis

Center theme 2: Understand Lignocellulose assembly

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

CSC structure: Crystallize the catalytic core of cellulose synthesis protein systems and develop a structural model; Identify novel components of the CSC in Arabidopsis and other organisms by biochemical and genetic approaches. Label components of the CSC with fluorescent tags and assess potential interactions of CSC components using fluorescence energy transfer methods. Work with modelers to incorporate all proven aspects of CSC structure and operation into their emerging models; Apply freeze fracture transmission electron microscopy to visualize the CSC and, possibly, sites of microfibril extrusion in protoplasts; carry out parallel work for the bacterial CSC. Develop *Physcomitrella* as a model system for studying CSC assembly and functions of specific molecular components.

Nanoengineering: Reconstitute partial or complete cellulose synthases, from plant or bacterial sources, in artificial membranes assembled within nanotube and nanomembrane arrays; 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 computational model of protein 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. Modify the crystallinity of cellulose through genetic modifications and through the introduction of hemicelluloses, to assess the mechanism of microfibril assembly and its impact on cellulose digestibility by defined cellulases.

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

Binding studies: Characterize the dynamics and energetics of specific cellulose-polysaccharide-protein-lignin binding interactions using isothermal titration calorimetry 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. Use defined Arabidopsis mutants and specific enzymes to test models of cell wall structure and its control of cell wall rheology. 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. Perform computational modeling of interactions and assembly of binary wall components.

Cell wall assembly and structural properties: Analyze cell wall mechanical properties and their dependence on cell wall composition/structure and their modification by endoglucanases, xylanases and other cell wall-loosening enzymes, using atomic force microscopy, extensometry and spectroscopic methods. Identify novel proteins that interact with glycosidases and lignin pathway enzymes upregulated in poplar wood-forming tissue. Develop model 3D synthetic plant cell wall systems implementing aligned cellulose fibrils in a flow cell, and use it to assess the impact of matrix polymers on assembly. Develop a plant protoplast model system for studying the initial stages of cellulose synthesis, cellulose structure, and cell wall assembly in Arabidopsis and *Populus* cells.

Spectroscopy and scanning probe microscopy studies: Elucidate cellulose-matrix interactions with experimental and computational IR using models generated by the center to address issues such as the site of binding to cellulose (crystalline or amorphous domains). Develop and test novel nonlinear spectroscopic methods to analyze cellulose structure in situ. 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.

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. Perform computational multiscale modeling with application to structural, mechanical, thermal and transport properties/processes. Extend atomistic modeling to larger length and time scales by use of a coarse-grained model which incorporates atomistic detail; Develop a coarse grained simulation model for cellulose structure and crystallization. Identify 4-5 model structures for study using small angle neutron scattering. Develop improved method to visualize lignin in the cell wall. 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), Nicole Brown, John Carlson, Jeffrey Catchmark, Vincent Crespi, Ying Gu, James Kubicki, Teh-hui Kao, Seong Kim, Janna Maranas, Virendra Puri, Tom Richard, Ming Tien, Bernhard Tittmann, Linghao Zhong
North Carolina State University	**Candace Haigler (Associate Director)**, Alex Smirnov, Yaroslava Yingling
Virginia Tech University	Alan Esker

Contact: Daniel Cosgrove, Eberly Chair and Professor of Biology; dcosgrove@psu.edu; (814) 863-3892
http://www.lignocellulose.org

Combustion Energy Frontier Research Center (CEFRC)

EFRC Director: Chung K. Law

Lead Institution: Princeton University

Mission Statement: To develop a validated, predictive, multi-scale combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications.

Technical Summary: As the world transitions away from petroleum-derived transportation fuels, the diversity of alternative fuels, particularly biomass-derived fuels, together with simultaneous changes in energy conversion device design/control strategies, pose immense technical challenges. Combustion of the new fuels is governed by coupled chemical and transport processes at multiple length and time scales ranging from electron excitation to molecular rearrangements to nanoscale particulate formation to turbulent fuel/air mixing. As such, satisfactory utilization of these alternative fuels to achieve improved efficiency and reduced emissions require coordinated efforts by researchers in the diverse disciplines of quantum chemistry, chemical kinetics, reactive flow simulations and experimentation, high-performance computation, and advanced diagnostics – expertise provided by the 15 principal investigators of the CEFRC.

The CEFRC has selected bio-butanol as the immediate fuel of investigation because, compared to ethanol which is the dominant bio-fuel presently marketed, bio-butanol has higher energy content, mixes well with gasoline, is not corrosive, and is under active development by energy and chemical industries for commercialization. A major advance since inauguration of the Center has been the development of the first-generation reaction mechanism describing the oxidation and pyrolysis of butanol at elevated pressures relevant for engine combustion, and validation of this new model in many different experiments. Notable advances are the following:

Theory of Reactions

- Development and validation of a high-accuracy *ab initio* quantum mechanics method suitable for studying bond-breaking in large molecules.
- New method developed for accurately modeling effects of multiple conformations on kinetics.
- Development of empirically-corrected DFT methods that achieve high accuracy at very low CPU cost.
- Identification of the decomposition routes of the radicals from the H-abstractions of small alcohols.
- Studies of collisional energy transfer crucial in determining pressure-dependent rate coefficients.

Development of Reaction Mechanisms

- Detailed probing of the combustion chemistry of biofuels by using the major classes of experimental instrumentation: shock tubes, variable-pressure turbulent flow reactors, rapid compression machines, low-pressure burner stabilized flames, and counterflow premixed and diffusion flames coupled with advanced laser diagnostics and synchrotron photoionization mass spectrometry, allowing access to a wide range of pressures, temperatures and stoichiometries for probing combustion reaction chemistry.
- Construction of a detailed chemical kinetics model for combustion of all four butanol isomers, tested against the literature data as well as data measured by other members of the CEFRC team.
- Kinetic models of propanol isomers and methyl butanoate are updated.
- Kinetic model for the H_2/O_2 system has been updated to predict burning rates at high pressures.
- Chemistry and kinetics of sooting processes in *n*-butanol and *i*-butanol have been examined.

- Mathematical and numerical procedure for kinetic parameter uncertainty quantification, propagation and minimization has been developed for combustion modeling over a large range of length and time scales.

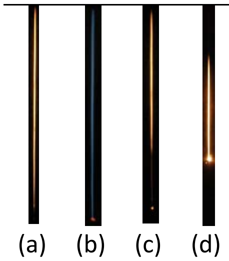
Chemistry/Transport Coupling

- Experimental data of laminar flame speeds, extinction/ignition limits, and soot/NOx emissions measured for hydrogen, C1-C7 hydrocarbons, C1-C4 alcohols, C1-C10 methyl-esters, and some important ethers, aldehydes, and ketones up to 25 atm. Kinetics models and transport properties of these fuels have been validated and improved.
- An efficient multi-timescale model reduction method has been developed and applied to direct modeling of homogeneous charge compression ignition (HCCI) combustion.
- A new combined method using large eddy simulation (LES), probability density function (PDF), and *in situ* adaptive tabulation (ISAT) to include the turbulence-chemistry interactions and to enable the efficient implementation of detailed mechanisms in turbulent flame simulations was developed.
- Direct numerical simulation (DNS) of the effect of thermal and concentration stratification in turbulent HCCI combustion for n-heptane and dimethyl ether was performed and analyzed.

Blending Strategy of Biodiesel, Diesel, and Ethanol

- A strategy of blending ethanol and biodiesel in diesel has been developed to synergistically moderate the soot emission propensity of diesel and the non-volatility of biodiesel. The concept capitalizes on the low-sooting property of biodiesel and the volatility of ethanol, resulting in the soot reduction through chemical interaction and improved atomization through the substantial volatility differential between ethanol and biodiesel. Such blending strategies hold promise for the design of future clean-burning and robust bio-fuels synthesized from a wide stream of bio-feedstocks.

Flame streaks of streams of burning droplets of various compositions



a) Diesel, showing yellow, sooty flame
b) Biodiesel, showing blue, non-sooty flame
c) 50-50% Diesel-biodiesel, showing reduced soot
d) 50-50% Diesel-ethanol, showing droplet explosion and hence facilitated gasification

COMBUSTION ENERGY FRONTIER RESEARCH CENTER (CEFRC)	
Princeton University	Chung K. Law (Director), Emily A. Carter (Co-Director), Frederick L. Dryer, Yiguang Ju
Argonne National Laboratory	Stephen J. Klippenstein
Cornell University	Stephen B. Pope
Massachusetts Institute of Technology	William H. Green
Sandia National Laboratories	Jacqueline H. Chen, Nils Hansen
Stanford University	Ronald K. Hanson
University of Connecticut	Chih-Jen Sung
University of Minnesota	Donald G. Truhlar
University of Southern California	Fokion N. Egolfopoulos, Hai Wang
University of Wisconsin – Madison	Rolf Reitz

Chung K. Law; Director, CEFRC; cklaw@princeton.edu; 609.258.5271; http://www.princeton.edu/cefrc/

Center for Direct Catalytic Conversion of Biomass to Biofuels (C^3Bio)
EFRC Director: Maureen McCann
Lead Institution: Purdue University

Mission Statement: C3Bio will develop transformational knowledge and technologies to optimize the energy and carbon efficiencies of conversion of biomass to advanced biofuels by the synergistic design of plant biomass and the physical and chemical conversion processes.

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. Lignocellulosic biomass is an annually renewable resource of home-grown energy available from U.S. agriculture and forestry. Second-generation biofuels are being 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. In contrast, the power of chemical catalysis to transform biomass components to advanced biofuels, similar in composition to gasoline or aviation fuel, and useful co-products for the petrochemical industry, 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.

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 requiring the development of catalytic deoxygenation chemistry and selective bond breaking to enable efficient transformations of lignin and polysaccharides to useful products. We are investigating homogeneous catalysts in condensed phase starting with simple models of monomers and dimers and building 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 are developing catalysts for selective hydrogenation of lignin, investigating bio-inspired selective oxidative dealkylation of lignin that targets specifically the benzylic group, and establishing tandem catalytic reactions for deoxygenation of polyalcohols, derived from cellulose and xylan in intact biomass. With the same range of biomass materials, we are studying 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 is enabling rapid molecular-level characterization of complex mixtures of reaction products. Underpinning the experimental approaches is 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 are developing 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 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 are being 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 genetics and molecular biology have enabled a revolution in our ability to produce plants with modified characteristics. We are investigating delivery of metal catalysts throughout the cell wall structure and creation of functionalized sites primed 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 novel catalysts and reaction chemistry for conversion of biomass to liquid fuels and chemical feedstock. The long-range impact of 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 that retain the current liquid fuel infrastructure and to other high-value hydrocarbon products.

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
Argonne National Laboratory	I. McNulty
University of Tennessee	J. Bozell, C. Barnes, A. Buchan
Northeastern University	L. Makowski

Contact: Maureen C McCann
Professor and Assistant Head of Biological Sciences, and Director of Purdue Energy Center
mmccann@purdue.edu, 765-496-1779, http://c3bio.org

Energy Frontier Research Center for Solid-State Lighting Science (SSLS)
EFRC Director: Michael E. Coltrin
Lead Institution: Sandia National Laboratories

Mission Statement: Exploring energy conversion in tailored photonic structures and materials to enable revolutionary breakthroughs in the efficiency and performance of LED-based lighting.

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. We have organized the EFRC into three scientific Thrusts. Within each Thrust are specific research projects, which we refer to as "Challenges."

Our first scientific Thrust is: **"Competing Energy Conversion Routes in Light-Emitting InGaN."** In this Thrust, we are studying wide-bandgap materials and the complex interplay between their defect and luminescent properties. The first Challenge within this Thrust is "Point Defects in InGaN: Microscopic Origin and Influence on Luminescence," in which we seek to understand the relationship between specific material defects, their dependence on various synthesis conditions, and the production or suppression of InGaN luminescence. The second Challenge is "Radiative and Non-Radiative Processes in the High-Carrier-Density Regime," 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 very poorly understood.

Our second scientific Thrust is **"Beyond Spontaneous Emission."** In this Thrust, we are studying energy conversion routes in subwavelength photonic structures in which electromagnetic fields are stronger or more localized, and photonic densities of states can be 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 are exploring strong coupling between excitons and photons in optical microcavities containing active wide-bandgap GaN-based materials. The second Challenge is "Surface Plasmonic Intermediaries to Exciton-Photon Interactions," in which we are exploring 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.

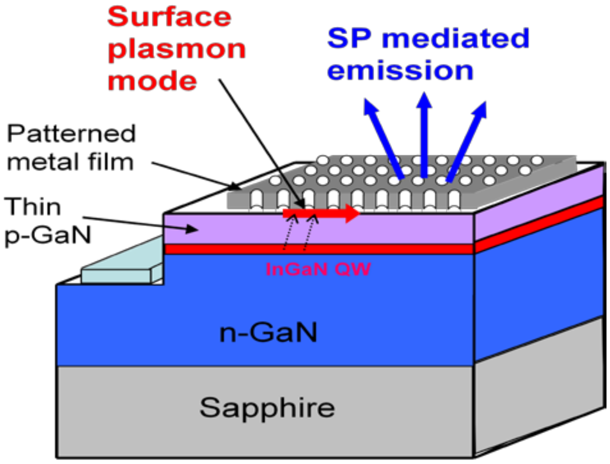


Figure 1. Plasmonic LED structure.

Our third scientific Thrust is **"Beyond 2D."** In this Thrust, we 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 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 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.

Throughout this EFRC, our emphasis is on fundamental science enabled by integrated, interdisciplinary capabilities: linking state-of-the-art nano-materials design, synthesis and characterization; linking theory and experiment; and linking scientific understanding of isolated phenomena studied in model systems with empirical observations that are found in relevant technology platforms. Advances in nano-fabrication and nano-characterization 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 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	
Sandia National Laboratories	M. E. Coltrin (Director), J. Y. Tsao, J. A. Simmons, G. T. Wang, A. J. Fischer, M. H. Crawford, A. Armstrong, J. E. Martin, E. A. Shaner, R. M. Biefeld, I. Brener, W. Chow, J. Huang, D. Koleske, F. Leonard, Q. Li, T. S. Luk, N. Modine, M. Nyman, L. Rohwer, G. Subramania, J. Wierer
Rensselaer Polytechnic Institute	E. F. Schubert
University of New Mexico	S. R. J. Brueck
Northwestern University	L. J. Lauhon
University of California, Irvine	K. Lyo
University of California, Merced	D. Kelley
University of California, Santa Barbara	J. Speck
Los Alamos National Laboratory	R. Prasankumar
Philips Lumileds Lighting	T. Mihopoulos, P. Grillot
California Institute of Technology	H. Atwater

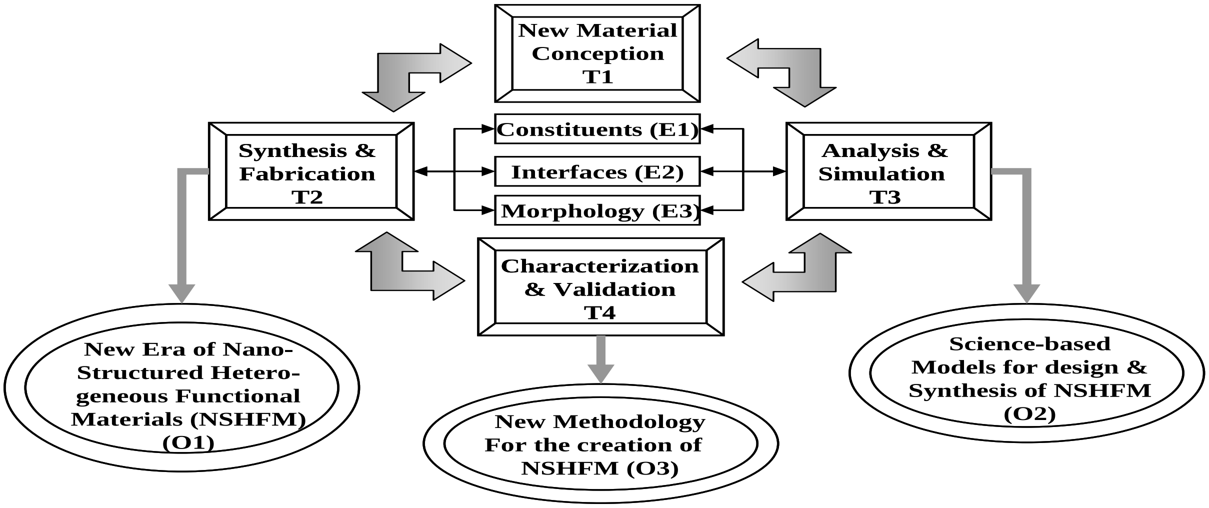
Contact: Michael E. Coltrin
mecoltr@sandia.gov
(505) 844-7843
http://ssls.sandia.gov/

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 is 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 is 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 are made available to the outside community of engineering and device designers (O1). On the right, models and simulations are 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) are 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 proposed 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 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.

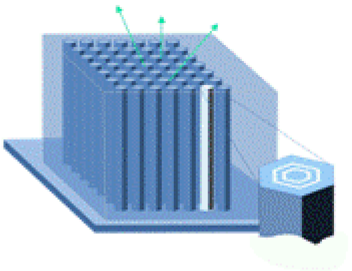
Heterogeneous Functional Materials Center (HeteroFoam)	
University of South Carolina	K. Reifsnider (Director), F. Chen, X. Xue, H. Zur Loye, A. Heyden
Georgia Institute of Technology	M. Liu, M. El-Sayed
Rochester Institute of Technology	D. Cormier
Princeton University	E. Carter, M. Haataja
University of California Santa Barbara	R. McMeeking
University of Connecticut	W. Chiu
University of Utah	A. Vikar, F. Liu
Savannah River National Laboratory	K. Brinkman

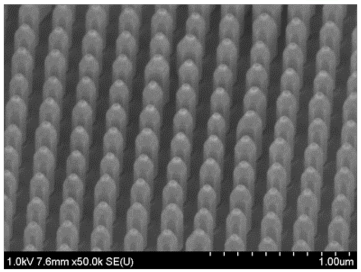
Contact: Ken Reifsnider
Director, SOFC Center of Excellence
Reifsnider@cec.sc.edu
(803)777-0084; -6450
http://hydrogen.csd.sc.edu/heterofoam

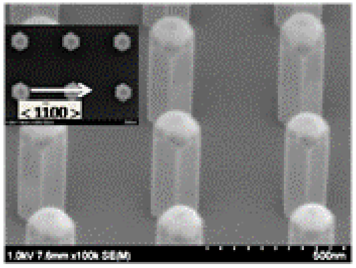
Center for Energy Nanoscience (CEN)
EFRC Director: P. Daniel Dapkus
EFRC Lead Institution: University of Southern California

Mission Statement: The Center for Energy Nanoscience seeks to transform the science and technology of low cost, high efficiency solar cells and light emitting diodes (LEDs) by exploring the physics, chemistry and properties of organic and nanostructure materials for these applications. CEN's scientists will create innovative materials and novel device designs based on new understanding of the fundamental properties of these materials that influence device performance.

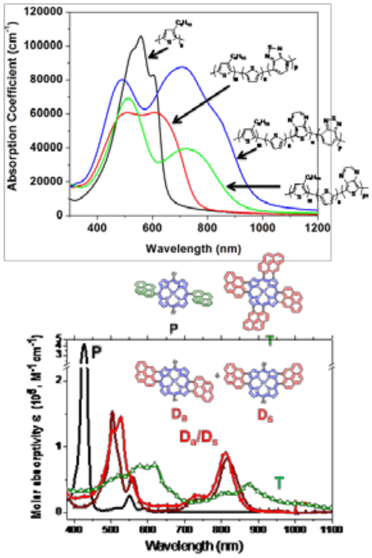
The Center for Energy Nanoscience program to explore emerging materials in solar energy and solid state lighting has as its goals the invention of new solar cell and LED designs based on nanostructured and organic materials. This program is motivated by the following vision: ***to demonstrate new technologies 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, nanoscale and femtosecond optical and transport characterization of molecular structures and 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 ultant 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.





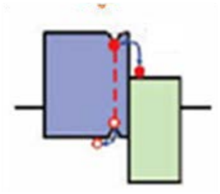


The objectives of our research during the first five years will be to develop the fundamental control at the atomic/molecular scale, the understanding of materials properties and processes at that level to permit the rational design of solar cells and LEDs based on these novel materials, the understanding 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.



Broadened spectral absorption in polymers (top) and small molecule (bottom) organic materials achieved by rational design.

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 to 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 technologies can be addressed by adopting the philosophy underlying our program. The major challenge to the economical implementation 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 characteristics, 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

Emerging Materials for Solar Energy Conversion and Solid State Lighting	
University of Southern California	P.D. Dapkus (Director), M. E. Thompson, A. V. Benderskii, S. E. Bradforth, R. L. Brutchey, S. B. Cronin, A. Krylov, J. G. Lu, A. Nakano, M. Povinelli, J. D. O'Brien, G. Ragusa, B. C. Thompson, W. Wu , C. Zhou
University of Illinois at Urbana-Champaign	J. J. Coleman
University of Michigan	S. R. Forrest
University of Virginia	J. C. Campbell

Contact: P. Daniel Dapkus
W. M. Keck Professor of Engineering
dapkus@usc.edu
213-740-4414
www.cen-efrc.org

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 how nanostructuring can enhance efficiency for energy conversion and solve cross-cutting fundamental problems in advanced energy conversion and storage systems.

The overarching goal of the Center is to increase the efficiency of energy conversion devices by manipulating materials at the nanometer scale. We 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 is manipulated to improve performance and efficiency in energy conversion and storage devices. Our research aims to 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 supports three thematic research thrusts:

- Nanoscale Control of Thermodynamic Potentials (TRG1)
- Nanoscale Control over Photons and Electrons (TRG2)
- Nanoscale Control in Catalysis (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 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 storage, and catalytic activity that are critically important for many energy conversion systems. We 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.

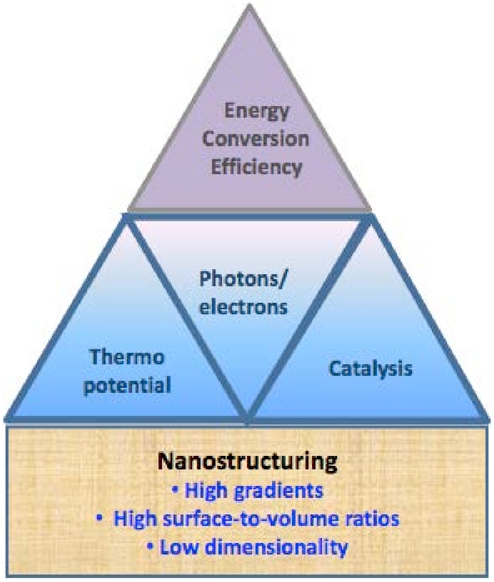


Figure 1. CNEEC concept and approach for improving energy efficiency.

Based on such fundamental work, we build and test structures that demonstrate how our fundamental advances can improve the efficiency of devices designed to convert solar energy and store it in usable forms (both electricity and fuel), as well as the rates associated with these conversion and storage processes. The nanoscale design principles we pursue 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.

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

Nanoscale Control of Thermodynamic Potentials (TRG1): ***Conversion efficiency is highest near thermodynamic equilibrium. Virtually any deviation from equilibrium results in irreversible energy losses. Energy conversion at practical rates requires conditions removed from equilibrium that result in losses associated with finite rates for kinetic and transport processes, which in turn reduce efficiency. We aim to improve energy efficiency by manipulating thermodynamic potentials such as induced fields that can result from a high surface-to-volume ratio at nanoscale sizes, thereby influencing the charge density and free energy of surface-bound chemical and electrochemical reactions.***

Nanoscale Control over Photons and Electrons (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. Nanostructuring enables the decoupling of photon absorption from charge collection processes as well as efficient trapping and concentrating of light. Quantum confinement structures, in which the size influences the electronic properties, allow us to tune the interaction of light and electrons, and to control the probability of electronic transition from a substrate to an adsorbate. Quantum confinement thus allows us to control properties such as light absorption and catalysis, which are important for photovoltaic (PV) and photoelectrochemical (PEC) devices.*

Nanoscale Control in Catalysis (TRG3): *To improve the efficiency of next generation energy conversion and storage devices, we must understand catalysis on nanostructured surfaces and interfaces and learn to control charge transport phenomena at interfaces. 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 understanding and controlling catalysis at the nanoscale and reducing the charge transport length.*

These properties – thermodynamics potentials, photonics, transport and catalysis – collectively 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 aims to 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 of new materials and structures as well as their synthesis, characterization, simulation, and device fabrication. Our partners 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 experimentation and synthesis. 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)	
Stanford University	**S.F. Bent and F.B. Prinz (co-Directors)**, M.L. Brongersma, B.M. Clemens, Y. Cui, D. Goldhaber-Gordon, T.F. Jaramillo, J. Nørskov, R. Sinclair, X.L. Zheng
Carnegie Institution	A.R. Grossman
Danish Technical University	K. W. Jacobsen
HRL Laboratories	P. Liu, J.J. Vajo

Contact: Prof. Stacey Bent; sbent@stanford.edu; (650) 723-0385; http://cneec.stanford.edu/

Northeastern Center for Chemical Energy Storage (NECCES)
EFRC Director: M. Stanley Whittingham
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 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 identify critical structural and physical properties that are vital to improving battery performance; and 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 and model single particle nano- and 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 is being 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 (Figure 1) is being used.

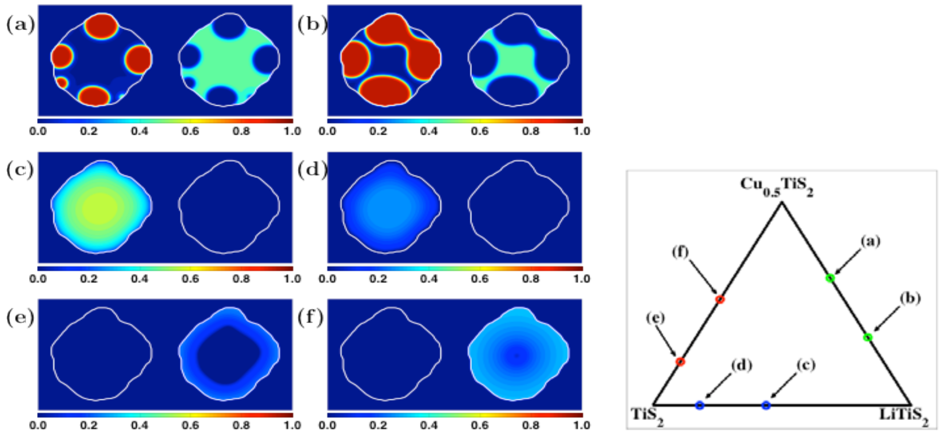


Figure 1: The concentration evolutions of Li (left side in each panel) and Cu (right side in each panel) during Li insertion ((a)-(b)), Li extraction ((c)-(d)), and Cu insertion ((e)-(f)). The corresponding points on the Gibbs ternary phase triangle are shown on the right.

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. Cross-over reactions, where the initial reaction is intercalation and the subsequent conversion are also being studied. These will, where possible, be performed in-situ so as to study the dynamic system, rather than after relaxation. 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 of this thrust is 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.

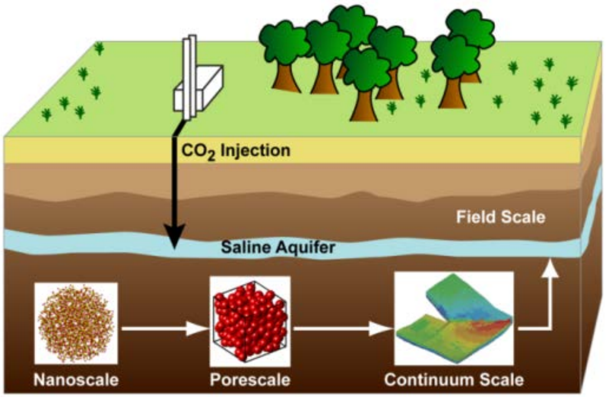
Northeastern Center for Chemical Energy Storage (NECCES)	
Stony Brook University	M.S. Whittingham (Director), C. P. Grey (Assoc. Director, Thrust 3 leader), P. Khalifah
Rutgers University	G. Amatucci (Assoc. Director, Thrust 4 leader) S. Garofalini, F. Cosandey, R. Bartynski
Binghamton University	M.S. Whittingham
Massachusetts Institute of Technology	G. Ceder (Thrust 2 leader)
Lawrence Berkeley National Laboratory	R. Kostecki (Thrust 1 leader), J. Cabana
Argonne National Laboratory	P. Chupas
Brookhaven National Laboratory	J. Graetz and X.-Q. Yang
U. C. San Diego	Y. S. Meng
University of Michigan	A. Van Der Ven and K. Thornton

Contact: M. Stanley Whittingham; stanwhit@gmail.com; 1(631)632-5724;
http://necces.chem.sunysb.edu/

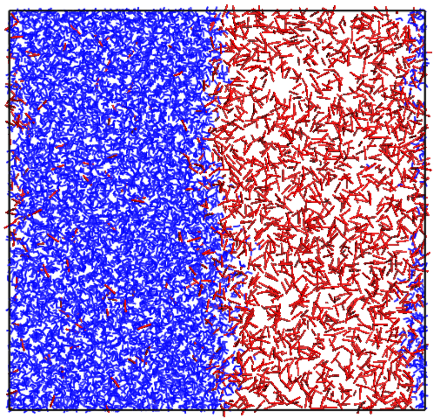
Center for Frontiers of Subsurface Energy Security (CFSES)
EFRC Director: Gary A. Pope
Lead Institution: The University of Texas at Austin

Mission Statement:

The Center for Frontiers of Subsurface Energy Security (CFSES) is pursuing scientific understanding of multiscale, multiphysics processes to successfully predict the behavior of CO_2 and other byproducts of energy production stored in the subsurface. We are integrating and expanding our knowledge of physical, chemical and biological processes from the molecular to the field-scale across using both experimental and modeling approaches to better understand and quantify behavior far from equilibrium. Ultimately, we will obtain capabilities to better predict long term behavior of subsurface storage.



The secure sequestration of energy byproducts, such as CO_2, requires improved scientific understanding from the nano to pore to field scales.



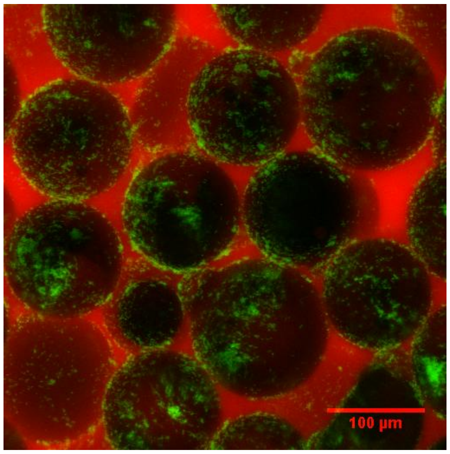
Molecular dynamics simulation showing interface between H_2O (blue) and CO_2 (red).

Project Description:

The subsurface disposal or storage of energy production waste materials entails time spans that are short compared to those of geological processes. The result is a highly perturbed system in which the chemical, biological, and physical reactions are significantly different from those observed in the natural state. Therefore, any comprehensive research program attempting to understand those processes must consider the coupled multiphysics driving active subsurface processes over broad spatial and temporal scales.

CFSES seeks to gain the necessary scientific understanding through a comprehensive and integrated research program focused on the key coupled process at different scales progressing from the molecular to field scale. The research conducted at CFSES capitalizes on the partnership of two world-class research institutions: The University of Texas Austin and Sandia National Laboratories. The research benefits from the unique resources, research capabilities, and facilities at both institutions. The research emphasizes the multiphysics at multiscales to:

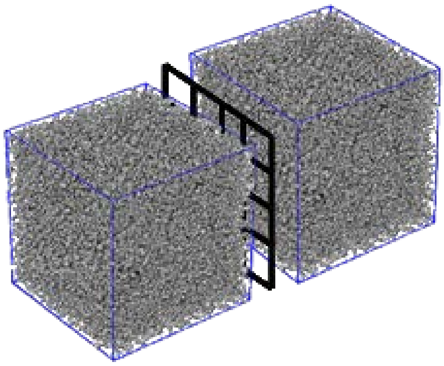
- Understand the interface between CO_2 and H_2O and other mineral surfaces
- Understand the impact of CO_2 and pH change on biomass distribution and flow properties
- Understand coupled mechanics, multiphase flow, and reactive transport



Confocal image of bacteria (green) growing on glass beads.

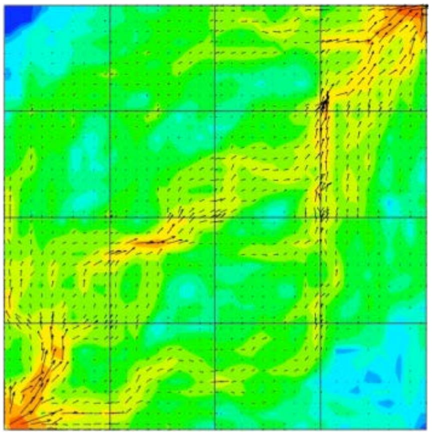
Numerical tools are being developed to:

- Conduct relevant molecular dynamics simulations
- Model fluid flow and reactive transport at the pore scale
- Model flow in faults and fractures
- Upscale pore-scale features to large heterogeneous network models
- Make long term predictions of flow and transport at the reservoir scale
- Assess the fate of injected CO_2
- Develop cutting edge techniques for coupling critical phenomena across scales

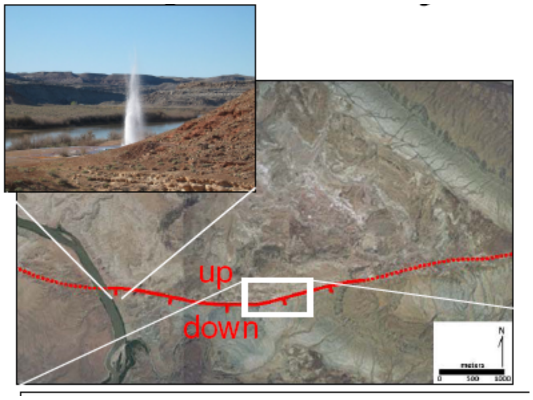


Using FEM mortars to link pore-level descriptions to continuum scale.

This research leverages information from natural analogs, such as the the Crystal Geyser site in Utah and current CO_2 injection experiments such as at the Cranfield, Frio, and Dickmans sites.



Multiscale flow simulation on coarse grids.



The Crystal Geyser natural analog site is being used to understand mechanisms for potential CO_2 leakage.

Center for Frontiers of Subsurface Energy Security (CFSES)	
The University of Texas at Austin	Gary Pope (Director), Mary Wheeler (Associate Director), Mojdeh Delshad (Assistant Director), Philip Bennett (Project Leader), Steven Bryant (Project Leader), Sanjay Srinivasan (Project Leader), Todd Arbogast (Project Leader), Matt Balhoff, Meinhard Bayani Cardenas, David DiCarlo, Peter Eichhubl, Marc Hesse, Susan Hovorka, Chun Huh, Keith Johnston, Larry Lake, Katherine Romanak, Mrinal Sen
Sandia National Laboratories	Marianne Walck (Associate Director), Susan Altman (Project Manager and Project Leader), Joseph Bishop (Project Leader), Thomas Dewers (Project Leader), Sean McKenna (Project Leader), Randy Cygan, Mario Martinez

Contact: Gary A. Pope, Director
gpope@mail.utexas.edu
(512) 471-3235
www.utefrc.org

Understanding Charge Separation and Transfer at Interfaces in Energy Materials (EFRC:CST)

EFRC Director: Peter J. Rossky

Lead Institution: University of Texas at Austin

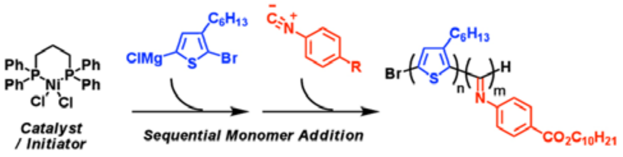
Mission Statement: The EFRC: CST aims to elucidate the critical interfacial charge separation and charge transfer processes that underpin the function of highly promising molecular materials for two energy applications: organic photovoltaics (OPV) and electrical energy storage (EES).

Solar energy conversion and storage are two critical components of a future strategy to achieve U.S. energy security. This EFRC focuses on a fundamental scientific challenge associated with the development of both OPV and EES technologies: understanding interfacial charge separation and transfer processes in nanostructured materials. Progress to date in this area has been limited owing to two major difficulties. The first difficulty is the structural complexity of materials on multiple length scales (nano, meso, and bulk scales) and the inaccessibility of these material interfaces to conventional probe techniques; this intrinsic difficulty has hindered the establishment of structure-property relationships in nanostructured materials for both OPV and EES applications. The second difficulty stems from the lack of reliable theoretical methodologies for describing interfacial charge separation and transfer dynamics in nanostructured materials. This unique size scale demands the bridging of two traditional theoretical models: one dealing with localized and molecular systems and the other dealing with delocalized and condensed phase systems. The EFRC:CST was established specifically to overcome these two difficulties and to critically advance the fundamental understanding of charge separation and transfer processes in nanostructured materials through three highly coordinated and focused scientific approaches:

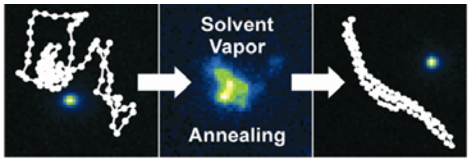
- Approach 1: The EFRC:CST supports a set of coordinated research projects focused on the design and synthesis of model interfacial prototypes that climb the ladder of complexity from single molecules and single crystals to bulk heterojunctions. These model systems serve as the basis for a divide-and-conquer strategy in experimentally and theoretically unraveling the complex charge separation and transfer mechanisms in nanostructured materials.
- Approach 2: The EFRC:CST is developing state-of-the-art imaging and spectroscopic tools, ranging from single particle spectroscopy/microscopy to in-situ nonlinear optical spectroscopy, to make correlated measurements of structure and charge separation/transfer processes on the multiple size scales present in the model systems developed in Approach 1.
- Approach 3: The EFRC:CST is advancing theoretical and computational methods in the comprehensive calculation and modeling of interfacial charge separation and transfer mechanisms. In close correlation with Approaches 1 & 2, these theoretical/computational efforts provide insights into structure of nanomaterial systems, electronic properties at model interfaces, nonadiabatic charge transfer dynamics from molecules to extended solids, and rate processes at multiple material and length scales

To implement these approaches, we have structured the EFRC:CST into two general thrust areas combining both experiments and theory. Thrust I, **Designing CST Materials and Interfaces,** aims to design, synthesize, and characterize materials and interfaces that we will use to reduce the complexity of nanostructured OPV and EES materials into unambiguous and well-characterized model systems. Thrust II, **Understanding CST Mechanisms,** aims to measure and simulate charge separation and transfer dynamics in model systems that span structural and size scales from single molecules and single crystals to bulk heterojunctions.

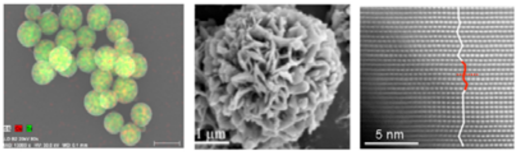
Thrust I: Designing CST Materials and Interfaces:



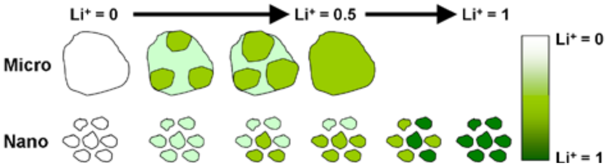
Polymer synthesis



Polymer morphology: experiments & modeling

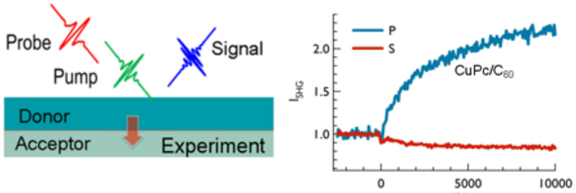


EES material synthesis & characterization

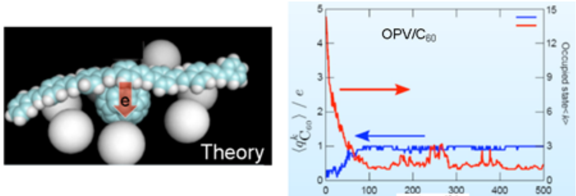


EES material modeling

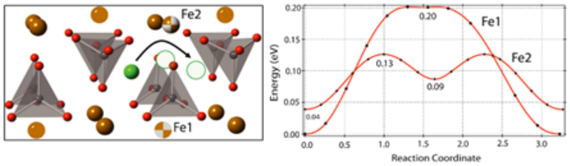
Thrust II, Understanding CST Mechanisms:



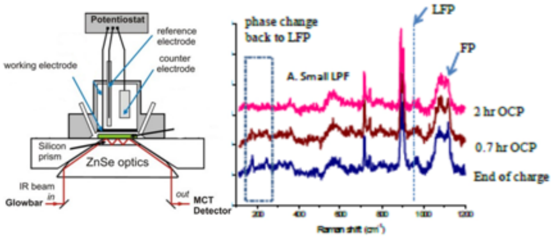
Charge separation dynamis from nolinear spectroscopy



Charge separation dynamics from theory



Li-diffusion from theory



In-situ Raman spectroscopy

Understanding Charge Separation and Transfer at Interfaces in Energy Materials (EFRC:CST)	
University of Texas at Austin	Peter J. Rossky (Director), A. J. Bard, C. Bielawski, A. Dodabalapur, P. Ferreira, V. Ganesan, J. Goodenough, G. Henkelman, B. A. Korgel, A. Manthiram, , K. J. Stevenson, D. A. Vanden Bout, L. J. Webb, X. Zhu
Sandia National Laboratories	K. Leung, C. Chan

Contact: Prof. Xiaoyang Zhu, Director
EFRC:CST
zhu@cm.utexas.edu
(512) 471-9914
http://www.efrc.nano.utexas.edu

Center for Catalytic Hydrocarbon Functionalization (CCHF)
EFRC Director: T. Brent Gunnoe
Lead Institution: University of Virginia

Mission Statement: To develop, validate, and optimize new methods to rearrange the bonds of hydrocarbons, implement enzymatic strategies into synthetic systems, and design optimal environments for catalysts that can be used to reversibly functionalize hydrocarbons, especially for more efficient use of natural gas including low temperature conversion to liquid fuels.

Fossil fuels, the dominant energy source in the United States, are primarily composed hydrocarbons. The current high temperature processes that convert these raw materials into useable forms lead to low efficiency, excessive emissions (including carbon dioxide) and a disproportionate dependence on imported petroleum. Due to the increasing demand for energy, current fossil fuel combustion processes will not adequately meet future energy needs. To provide for a secure energy future in the United States and worldwide, new technologies that revolutionize hydrocarbon utilization will be necessary.

Catalysts for the low temperature and selective functionalization of hydrocarbons are central to the development of advanced technologies that can provide dramatic improvements in the utilization of energy resources. For example, such systems could open new avenues for use of natural gas, provide cleaner and more energy efficient routes for hydrocarbon processing and lead to the development of high efficiency fuel cells. The Center for Catalytic Hydrocarbon Functionalization (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.

The development of efficient catalysts for the conversion of hydrocarbons into higher value materials 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 carbon-heteroatom bond, and c) release the functionalized product with protection against additional reaction. The CCHF will explore four areas for the development of novel catalysts:

1. New Methods for Carbon-Heteroatom Bond Formation

A primary focus of the CCHF is the controlled conversion of hydrocarbons to “functionalized” materials (*e.g.*, oxygenated compounds such as alcohols, Equation 1). The formation of carbon-heteroatom bonds is a major chemical challenge. For example, reacting metal hydrocarbyl complexes with oxidants to deliver new C-O bonds has been particularly difficult, especially when attempting to incorporate dioxygen as the oxygen atom source. Researchers in the CCHF will develop new pathways for these transformations and garner atomic level understanding of how the features of the metal work in concert with the oxidant to promote the reactions. The CCHF will focus on the design of new classes of organometallic complexes that react readily with oxygen sources, new methods to activate dioxygen, new technologies that permit controlled C-O bond formation, and computational methods capable of accurately predicting the best materials on which to focus the experiments.

$$\mathrm{R{-}H} + 1/2\,\mathrm{O_2} \xrightarrow{\mathit{Catalyst}} \mathrm{R{-}OH} \qquad (1)$$

2. New Classes of Metal Oxo Complexes

Nature functionalizes hydrocarbons using metal oxo complexes (*i.e.,* systems with M=O bonds, Figure 1) 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 very limited. The CCHF will pursue new strategies to synthesize systems that provide more controlled hydrocarbon functionalization chemistry. Efforts are directed toward: a) developing metal oxo complexes that can activate C-H bonds with bond dissociation energies > 95 kcal/mol, b) elucidating strategies to control radical reactivity via fast C-O bond forming rebound steps, and c) working to develop electrocatalysts that can convert water to reactive metal oxo complexes for C-H oxidation.

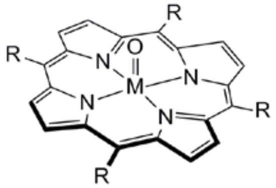


Figure 1. A generic high valent metal complex with a porphyrin ligand.

3. New Materials for C-H Functionalization

A substantial challenge for hydrocarbon functionalization is developing catalytic systems that react selectively with inert alkanes. New materials research in the CCHF is directed toward understanding and tailoring heterogeneous systems for C-H functionalization chemistry. Efforts in this area involve design and synthesis of unique nanostructured materials (Figure 2), work on the fringe of heterogeneous and homogeneous catalysis, and use of computational chemistry to understand, model, and predict reactivity.

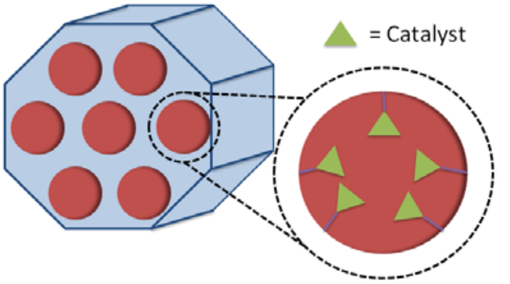


Figure 2. A schematic of catalyst attachment to a mesoporous nanoparticle.

4. The Development of Catalysts for Methane Fuel Cells

Current fuel cell technology is not suitably efficient, reliable, or economical to provide power to homes where natural gas is available. The key to low temperature methane fuel cells is the development of stable, efficient electrocatalysts with low overpotentials for the anodic oxidation of methane. Work in the CCHF seeks to combine expertise in homogeneous C-H functionalization, electrocatalysis, and computational chemistry to develop new catalysts for application in methane fuel cells.

Center for Catalytic Hydrocarbon Functionalization (CCHF)	
University of Virginia	T. Brent Gunnoe (Director), Cecelia Cropley (Scientific Program Administrator)
Brigham Young University	Daniel H. Ess
California Institute of Technology	William A. Goddard, III
Colorado School of Mines	Andrew Herring, Brian G. Trewyn
Princeton University	John T. Groves
The Scripps Research Institute	Roy A. Periana
University of Maryland	Andrei N. Vedernikov
University of North Carolina	Thomas J. Meyer
University of North Texas	Thomas R. Cundari
Yale University	Robert H. Crabtree

Contact: T. Brent Gunnoe, Director
tbg7h@virginia.edu, (434) 922-2692
http://artsandsciences.virginia.edu/cchf/

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

Mission Statement: PARC aims to understand the basic scientific principles that govern solar energy collection by photosynthetic organisms and plans to use this knowledge to enhance natural antenna systems and to fabricate biohybrid and bioinspired systems for light-harvesting.

Understanding the process of energy transfer is the central concept of PARC. Through basic scientific research, PARC seeks to understand the principles of light-harvesting and energy funneling as applied to three interrelated programmatic themes:

1. Natural Antennas: Structure and Efficiency
2. Biohybrid Antennas: Organization and Implementation
3. Bioinspired Antennas: Design and Characterization

Specific Goals for Theme 1: Natural Antennas: Structure and Efficiency

PARC seeks to understand the structure and function of the wide variety of natural photosynthetic antenna systems in molecular terms, including their efficiency, mechanism of action, regulation, assembly and repair. Particular emphasis will be placed on developing new and modified antenna systems using techniques of molecular and synthetic biology that increase the efficiency of living photosynthetic organisms by reducing light saturation effects and expanding the spectral ranges of radiation that can be used for energy storage. The specific goals are as follows:

1. To determine the molecular structures of native and modified antenna systems that correlate with function.
2. To understand the subcellular organization of antenna systems in different photosynthetic organisms.
3. To examine physiological consequences of modified/alternate antenna systems in diverse photosynthetic organisms.

The overall aim is to determine and manipulate the antenna size and composition to maximize photosynthetic efficiency in any such organism.

Specific Goals for Theme 2: Biohybrid Antennas: Organization and Implementation

PARC will develop the new research area of “bottom-up” fabrication of biohybrid antenna architectures, in which natural light-harvesting (LH) complexes are coupled to artificial substrates, and also in which artificial pigments are incorporated into natural antenna complexes. Particular emphasis will be placed on attachment chemistry, substrate properties, assembly, efficiency of energy delivery and stability. The specific goals are as follows:

1. To develop lithographic methods to pattern arrays of LH complexes, purified from bacterial photosynthetic membranes, on surfaces in a variety of geometries, including nanoscale lines, and dots.
2. To extend this approach initially to fabricate multi-component structures consisting of two, then three types of LH and/or reaction center complexes on a single surface to promote directed energy migration and trapping.
3. To further extend this approach to genetically and chemically modified, biohybrid molecules, employing designer proteins or pigments, and to use far-and near-field fluorescence microscopy for spectroscopic readout.

The overall aim is to design proof-of-principle biohybrid architectures for energy collection and storage.

Specific Goals for Theme 3: Bioinspired Antennas: Design and Characterization
PARC will draw upon the fundamental knowledge of native, biohybrid and synthetic antenna complexes, both architectures and processes, to design and assemble LH arrays to integrate into target solar-conversion systems. The ultimate aim is fabrication of LH assemblies that absorb 90% of the incident photons over any specified subset or full span of the 350 to 900 nm region of the solar spectrum, delivering the energy to a target site or sites where it is trapped with a quantum yield of 80% or greater. The assemblies will be stable over a timescale of months, and will expand the physical size of purely biological LH arrays ten-fold from 100-500 nm to 5000 nm. The specific goals are as follows:

1. To base self-assembling macromolecular arrays on tunable pigments incorporated into designer maquette polypeptides or engineered native antenna proteins.
2. To extend the functionality of the arrays to include sites of energy trapping and photochemistry at defined positions.
3. To control the mesoscale architecture of artificial assemblies using lithographic approaches to interface the synthetic and biohybrid components.

The overall aim is the fabrication of micron-scale arrays for efficient solar light harvesting, energy transfer and trapping that can be used for chemical processes or generation of photocurrent.

In order to accomplish PARC's goals, an integrated synergistic approach is essential when one considers the center's multiple personnel, geographically-dispersed partner institutions, and wide-ranging capabilities. In addition to the principal investigators listed below, PARC has implemented a robust Research Affiliate Program for establishing external collaborations and partnerships. There are currently 12 PARC Research Affiliates worldwide. Research Affiliate status is typically a non-monetary award except when PIs engage them in a specific PARC project (e.g., Paul Loach and Pamela Parkes-Loach at Northwestern University). Research Affiliates provide a valuable contribution to PARC's vision and strategy through ongoing support of the center's goals and by participating in center activities.

Other PARC personnel include five Scientific Advisory Committee members, 10 research/technical associates, 20 postdoctoral associates, 17 graduate students, and four undergraduate students.

Photosynthetic Antenna Research Center (PARC)	
New Mexico Consortium	R.E. Blankenship (Director), D. Holten (Associate Director and Theme 3 Leader), H. Pakrasi (Theme 1 Leader), P. Biswas, and C. Lo.
New Mexico Consortium	R. Sayre
Los Alamos National Laboratory	G. Montaño
North Carolina State University	J. Lindsey
Oak Ridge National Laboratory	D. Myles and V. Urban
Sandia National Laboratory	J. Timlin
University of California, Riverside	D. Bocian
University of Glasgow, UK	R. Cogdell
University of New Mexico	A. Shreve
University of Pennsylvania	P.L. Dutton and C. Moser
University of Sheffield, UK	N. Hunter (Theme 2 Leader)

Contact: Robert E. Blankenship, Lucille P. Markey Distinguished Professor of Biology & Chemistry
blankenship@wustl.edu; 314-935-7971; http://parc.wustl.edu/

GRAND CHALLENGES INDEX

BASIC RESEARCH NEEDS INDEX

TOPICAL INDEX

EXPERIMENTAL AND THEORETICAL METHODS INDEX