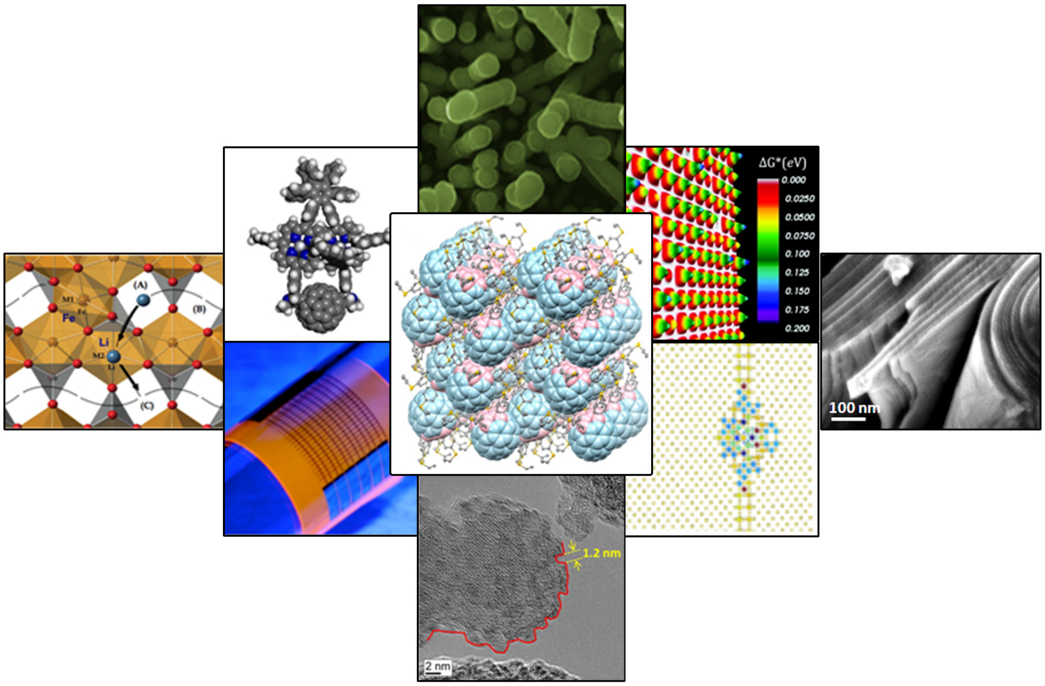
Energy Frontier Research Centers

Technical Summaries



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U.S. DEPARTMENT OF ENERGY | Office of Science

IMAGES ON THE FRONT COVER

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INTRODUCTION

Since their inception in 2009, the U. S. Department of Energy's Energy Frontier Research Centers (EFRCs) have become an important research modality in the Department's portfolio, performing high impact research that addresses key scientific challenges for energy technologies. Funded by the Office of Science's Basic Energy Sciences program, the 46 EFRCs are located across the United States and are led by universities, national laboratories, and private research institutions. These multi-investigator, multi-disciplinary centers have world-class teams of researchers, often from multiple institutions, bringing together leading scientists to tackle the toughest scientific challenges preventing advances in energy technologies. The EFRCs' fundamental scientific advances are having a significant impact that is being translated to industry. As of May 2012, the centers have authored over 2,400 publications in peer reviewed journals, have filed 55 invention disclosures and 124 patents/applications, and have issued at least 22 licenses for EFRC patents. According to the centers, more than 30 companies have benefited from the results of EFRC research, including both small start-ups and major corporations.

These technical research summaries, prepared by the EFRCs in August 2012, describe past and planned work as the EFRCs enter their fourth year of their five year award period; list all the partner institutions and the associated senior investigators; and provide self-identified 'grand challenges', 'basic research needs', topical, and experimental and theoretical methods keywords in the indices.

TABLE OF CONTENTS

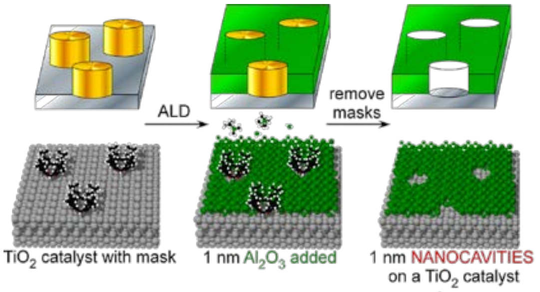
Ordered first by Institution and then by Director

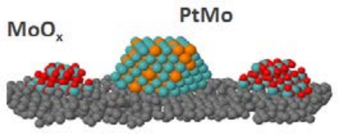
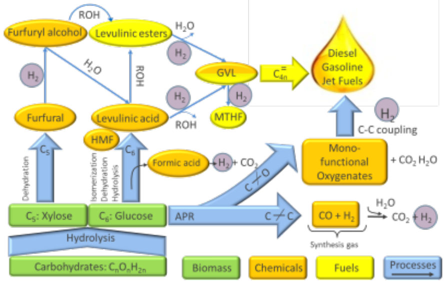
Institute for Atom-efficient Chemical Transformations (IACT)
EFRC Director: Christopher L. Marshall
Lead Institution: Argonne National Laboratory

Mission Statement: *To address key catalytic conversions that could improve the efficiency of producing fuels from biomass. IACT is focusing on advancing the science of catalysis for the efficient conversion of energy resources into usable forms. IACT's goal is to find ways to achieve control and efficiency of chemical conversions comparable to those in nature.*

Vision: The focus of IACT is to advance the science of catalysis for the efficient conversion of renewable energy resources into usable forms. IACT is a partnership among world-class scientists at Argonne National Laboratory, Northwestern University, University of Wisconsin-Madison, Purdue University, and Brookhaven National Laboratory. Using a multidisciplinary approach involving new catalyst synthesis, advanced characterization, catalytic experimentation, and computation, IACT addresses three catalytic conversions that are key to improving the efficiency for conversion of biomass to fuels: 1) selective removal of oxygen by dehydration, 2) selective hydrogenation of oxygen containing functional groups, and 3) C-C bond formation. The grand vision for IACT is to create a knowledge base for these key transformations that guides efficient deconstruction of biomass and enables highly selective conversion of the resulting oxygenated molecules to fuel components with minimum loss of the precious carbon that was fixed by photosynthesis to create the biomass. Thus, precise control of reaction pathways is our main mission.

To achieve this mission, IACT consists of four distinct, but intimately interlinked subtasks: synthesis, characterization, computation, and chemical and catalytic reaction science (see diagram on next page). The integration and interdependence of these subtasks follow naturally from the needs that each has for the others to answer basic scientific questions. This integration and interdependence are ensured by (i) an effective management structure, whose membership cuts across subtask expertise, and (ii) regular communication among participants via meetings, seminars, and collaborations.

Research Goals	**Key Progress Milestones**
Synthesis of nanobowls for the controlled catalysis and protection of small metal particles.  **Schematic for templated synthesis of nanobowls in an Al_2O_3 layer on a TiO_2 particle.**	• Established the shape- and size-selectivity of nanobowl catalysts prepared by templated ALD for the photocatalytic oxidation of alcohols. • Demonstrated enhanced thermal stability and selectivity of ALD over-coated noble metal nanoparticle catalysts.
Improved catalyst activity and selectivity for the reforming of small alcohols.	• Developed a series of highly active and stable bimetallic catalyst has been discovered which produces hydrogen from biomass under aqueous reaction conditions.

 **Alloying Pt with less noble metals (e.g. Mo or Co) improves activity and selectivity for aqueous phase reforming reactions.**	• Synthesized a highly active and selective new bimetallic catalyst has been discovered, which hydrogenates oxygen-rich biomolecules to gasoline-compatible fuels under aqueous reaction conditions.
Improved fundamental understanding in the catalytic conversion of furfural to levulinic acid.  **Overall scheme of reactions being explored within IACT for the conversion of cellulosic biomass to transportation fuels.**	• Identified that one of the major reaction pathways for conversion in liquid water of furfuryl alcohol to levulinic acid takes place via a geminal diol species formed by the addition of two water molecules. • Identified multiple reaction pathways for conversion of furfuryl alcohol in ethanol solvent to ethyl levulinate, one of which leads to the co-production of diethylether.
Selective conversion of glucose and fructose to chemical intermediates.	• Concluded a theoretical and experimental study of the pathways and intermediates for the conversion of fructose to hydroxymethylfurfural (HMF) in dimethyl sulfoxide. HMF is a desirable compound for further processing into chemical feedstocks. • Showed that high level calculations can provide detailed data on the energetics and pathways for a variety of relevant reactions including lactic acid hydrogenation to propylene glycol and propanoic acid on Pt(111), and the mechanism for furfural hydrogenation and decarbonylation on transition metal surfaces.

Institute for Atom-efficient Chemical Transformations (IACT)	
Argonne National Laboratory	Christopher L. Marshall (Director), Peter C. Stair (Deputy Director), Linda Broadbelt, Larry Curtiss, Jeffrey Elam, Jeffrey Miller, Randall Winans (Senior Investigators)
Northwestern University	Mayfair Kung, Tobin Marks, Justin Notestein, Kenneth Poeppelmeier, Peter Stair, Eric Weitz (Senior Investigators)
Purdue University	W. Nicholas Delgass, Jeffrey Greeley, Fabio Ribeiro (Senior Investigators)
University of Wisconsin	George Huber, James Dumesic, Thomas Kuech, Manos Mavrikakis (Senior Investigators)
Brookhaven National Laboratory	Eric Stach (Senior Investigator)

Contact: Christopher L. Marshall, Director – Institute for Atom-efficient Chemical Transformations (IACT)
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Center for Electrical Energy Storage (CEES)

EFRC Director: Michael Thackeray

Lead Institution: Argonne National Laboratory

Mission Statement: *To acquire a fundamental understanding of interfacial phenomena controlling electrochemical processes that will enable dramatic improvements in the properties and performance of energy storage devices, notably lithium-ion 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.

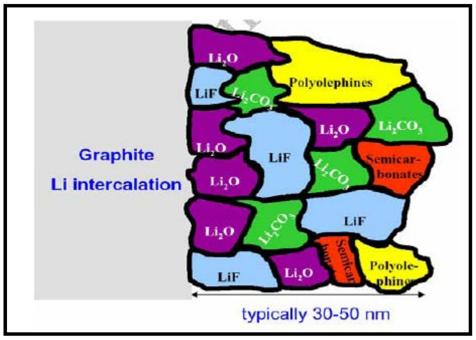

Figure 1. Schematic depiction of a solid-electrolyte interface ("SEI" layer)

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 (Institutional Lead), D. D. Dlott, J. S. Moore, R. G. Nuzzo, N. R. Sottos, S. R. White
Northwestern University	M. C. Hersam (Institutional Lead), M. J. Bedzyk, H. H. Kung, C. Wolverton

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http://www.anl.gov/energy-storage-science/

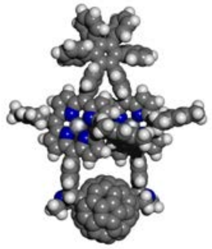
Center for Bio-Inspired Solar Fuel Production (BISfuel)
EFRC Director: Devens Gust
Lead Institution: Arizona State University

***Mission Statement**: To construct a complete system for solar-powered production of hydrogen fuel via water splitting. Design principles are drawn from the fundamental concepts that underlie photosynthetic energy conversion.*

Society's heavy reliance on fossil fuels is not sustainable, leads to a variety of geopolitical and economic problems, and contributes to climate change. Sunlight is the most promising renewable source of energy with the capacity to power the world's immense energy economy. The need for a continuous energy supply and energy requirements for transportation necessitate both storage of energy from sunlight in fuel and conversion to electricity. Cost-effective technologies for solar fuel production do not exist, prompting the need for new fundamental science.

Natural photosynthesis harvests solar energy on a scale much larger than that necessary to fulfill 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 carbohydrates, lipids, or molecular hydrogen. Photosynthesis is a practical, time-tested natural example of large-scale solar fuel production.

The BISfuel center's approach to the design of a complete system for solar water oxidation and hydrogen production follows the functional blueprint of photosynthesis using designed materials. Collection of sunlight and its conversion to electrochemical potential is performed by artificial antenna-reaction centers. These are constructed using the tools of organic chemistry and components such as porphyrins, fullerenes, and carotenoid polyenes. They incorporate light harvesting, charge separation, photoprotection and regulation. A variety of these have been prepared (an example is shown to the right).



An artificial photo-synthetic reaction center

Working together, BISfuel scientists from a variety of disciplines are pursuing a multi-track approach to creating catalysts. The Center has developed functional water oxidation catalysts using metals such as iridium and cobalt. A more biomimetic approach under investigation is based on a unique, self-assembling, engineered DNA nanostructure that organizes short synthetic peptides in a manner analogous to those in the natural oxygen-evolving complex. These peptides are being used to scaffold a manganese-based catalytic site similar to the natural one using assembly methods found in photosynthesis. In yet another method, peptide-organized water-soluble analogs of the natural photosynthetic oxygen-evolving complex are being developed.

The hydrogen production catalysts under development are synthetic molecules designed using first row transition metals and concepts from natural hydrogenase enzymes. Metal-containing catalytic sites and iron-sulfur sites for storing reduction equivalents are being organized into functional catalysts using synthetic peptides or other supramolecular approaches and interfaced to transparent electrodes.

New transparent, nanostructured, high-surface-area semiconducting porous metal oxide materials are being devised to serve as functional frameworks for organizing the components of the system, separating mutually reactive intermediates, and facilitating electrical communication among components. Several new methods of fabricating such materials have been developed thus far and the ability to incorporate functional molecules has been demonstrated.

DOE National Laboratory resources including SLAC at Stanford, NSLS, and the ALS in Berkeley are being used for X-ray, EXAFS, and electron paramagnetic resonance characterization of the artificial water oxidation and proton reduction catalysts. BISfuel has helped develop the revolutionary new tool of femtosecond X-ray crystallography of nanocrystals for determining the structures of complex and sensitive biological and non-biological molecular materials.

A major challenge is the integration of the various components mentioned above into a unified functional system that is competent to carry out solar-powered water splitting. This requires careful attention both to the thermodynamic and kinetic properties of the catalysts and charge-separation units and to the transport of electrons, protons and other materials among the various subsystems of the complex. Thus, the research has a strong systems engineering component. The Center has demonstrated a functioning system for solar water splitting in the laboratory, but much more research is necessary to evolve a practical process. BISfuel has determined that two photosystems in tandem, à la photosynthesis, will be necessary to achieve useful efficiencies, and such systems are being investigated. Based on the performance of natural photosynthesis, synthetic systems have 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.

While pursuing this ambitious goal, the Center is uncovering basic scientific knowledge that will point the way to new catalysts for 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 is also helping to identify ways to modify natural photosynthesis to satisfy better humanity's needs.

Success is possible only through close cooperation among BISfuel scientists from a wide variety of disciplines, including materials science, biochemistry, molecular biology, synthetic organic chemistry, inorganic and bioinorganic chemistry, biology, photochemistry and photophysics. Each BISfuel research subtask focusing on a component of the final system is itself multidisciplinary, and all subtasks 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, V. Mujica, K. Redding, D.-K. Seo, Ryan Trovitch, H. Yan

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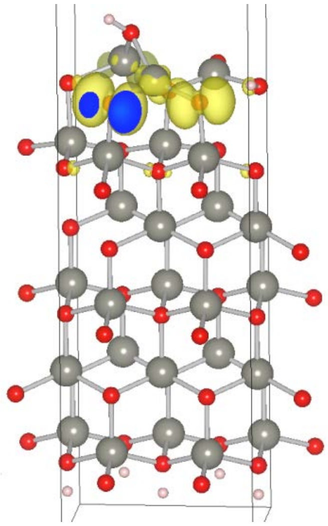
Center for Interface Science: Solar Electric Materials (CISSEM)
EFRC Director: Neal R. Armstrong
Lead Institution: The University of Arizona

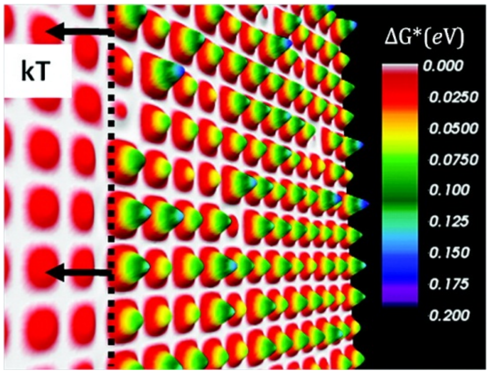
Mission Statement*: To advance the understanding of interface science underlying solar energy conversion technologies based on organic and organic-inorganic hybrid materials; and to inspire, recruit and train future scientists and leaders in the basic science of solar electric energy conversion*.

CISSEM was established in August 2009 as an Energy Frontier Research Center funded by the U.S. DOE, Office of Science, Office of Basic Energy Sciences, through Award Number DE-SC0001084. Under the Directorship of Prof. Neal R. Armstrong, The University of Arizona is teamed with the Georgia Institute of Technology, the National Renewable Energy Laboratory (NREL), Princeton University, and the University of Washington. CISSEM, an integrated multi-investigator five-year $15M program that started in August 2009, is comprised of fourteen principal investigators; with more than sixty graduate students, postdoctoral research associates, scientists, engineers, and staff involved with the center. We combine state-of-the-art facilities, leading researchers, and enthusiastic students to investigate the interface science of solar cell photovoltaics (PVs), building the basic science foundation and training the future energy scientists required to help develop abundant, clean, and economical energy conversion technologies for the 21st century.



Theoretical modeling – Charge distributions corresponding to the valence band maximum for a ZnO (0002) hydroxylated surface containing defects DOI: 10.1021/cm301596x

Interfacial processes are the focus of our collaborative and synergistic efforts. We are focused on understanding, modifying, and controlling the processes that affect efficiency in emerging thin-film PV technologies at nanometer length scales (one nanometer is about 1/100,000 of the width of a human hair). Regions called "interfaces" form where different materials contact each other. The chemical and physical processes that occur at interfaces control the efficiency, lifetime, and manufacturability of thin-film PVs, and must be understood and improved to support the desired growth of PV technologies (at well under $1/watt) and the U.S. renewable energy portfolio.

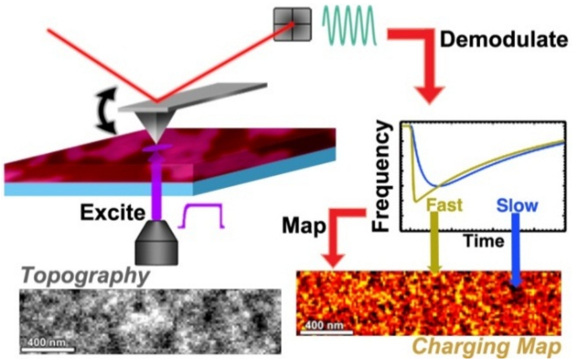


Kinetic Monte Carlo simulations – Free energy of activation (ΔG^*) calculations for electron transfer at the interface between an organic PV active layer and an electrode DOI: 10.1021/jp207471f

For Years 4 and 5, the CISSEM team is pursuing a unifying, vertically-integrated theme, using select combinations of model materials. We will create an understanding of the electronic properties of interfaces between molecular semiconductors and electrical contact or "interlayer materials" that lead to efficient harvesting of electrical charges, and describe their impact on thin-film PV performance. Consistent with our status as an EFRC, this research supports the development of high efficiency, stable, and scalable solar cell energy conversion platforms, and evolves from CISSEM's research activities in Years 1-3. An "interlayer" is a thin (1-50 nanometer) layer of metal oxide or polymer placed adjacent to a contact electrode in a thin- film solar cell. Its composition and structure enhances the efficiency of charge extraction and boosts PV efficiency.

CISSEM is:

- A multi-investigator center addressing the science of interfacial processes that limit efficiencies and lifetimes in emerging solar electric energy conversion technologies, which requires the characterization and control of these processes at nanometer length scales.
- 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, engaging the unique array of research facilities and expertise at CISSEM's universities and NREL.
- A research program creating new scientific understandings of the electronic properties of interfaces relevant to many complementary energy conversion systems including other thin-film PV platforms, energy storage systems, photoelectrochemical platforms that create fuels from sunlight, and new thin-film, solid-state lighting technologies.



Characterization – Schematic of the fast free time-resolved electrostatic force microscopy technique that maps electrical transients at ca. 100-200 nanosecond timescales (1000X faster than comparable methods) with ca. 80 nanometer resolution
DOI: 10.1021/nl203956q

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), Erin Ratcliff, S. Scott Saavedra (Associate Director)
Georgia Institute of Technology	Jean-Luc Brédas, Samuel Graham, Bernard Kippelen (Associate Director), Seth R. Marder (Associate Director)
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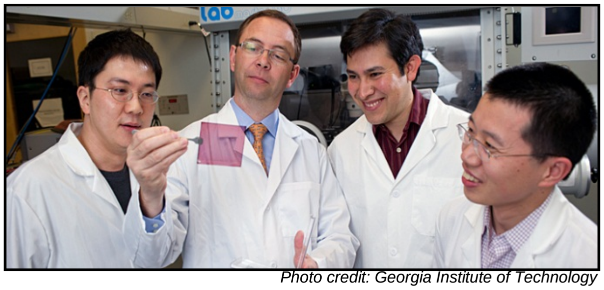

Use-inspired discoveries of basic phenomena – Georgia Tech researchers displaying an all-polymeric organic solar cell on a flexible substrate featuring a new polymer-based, electron-collecting electrical contact
DOI: 10.1126/science.1218829

Photo credit: Georgia Institute of Technology

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

***Mission Statement**: To discover new high-temperature superconductors and improve the performance of known superconductors by understanding the fundamental physics of superconductivity.*

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 including the cuprate superconductors and the Fe-based materials**, and **controlling vortex matter to raise the current carrying performance** of high temperature superconductors.

Center for Emergent Superconductivity (CES)	
Brookhaven National Laboratory	J. C. Séamus Davis (Director), Peter D. Johnson, John M. Tranquada, Cedomir Petrovic, John Hill, Alexei Tsvelik, Ivan Bozovic, Genda Gu, Qiang Li, Mark Dean
Argonne National Laboratory	George Crabtree, Mike Norman, J.C. Campuzano, Wai Kwok, Alexei Koshelev, Duck-Young Chung, Vitalii Vlasko-Vlasov, Ulrich Welp, Mercouri Kanatzidis
University of Illinois, Urbana-Champaign	Laura Greene, Anthony J. Leggett, Dale Van Harlingen, Peter Abbamonte, Jim Eckstein, Philip W. Phillips, Jian-Min Zuo, Raffi Budakian, Russell W. Giannetta
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Light-Material Interactions in 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 to sculpt the flow of sunlight, enabling light conversion to electrical and chemical energy with unprecedented efficiency.*

The Light-Material Interactions in Energy Conversion Energy Frontier Research Center (LMI-EFRC) is 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 of researchers that spans the campuses at California Institute of Technology, Lawrence Berkeley National Laboratory, and University of Illinois at Urbana-Champaign. This Center is a foundational partnership between scientific world leaders in optical properties of matter with internationally recognized experts in photovoltaic energy conversion and innovators in the design and fabrication of novel electronic and photonic materials. We are creating new methods and architectures for complex photonic materials for solar energy conversion, including metamaterials, transformation optics, plasmonics, photonic crystals and other dielectric spectrum-splitting and light-trapping elements. These structures span dimensions ranging from the greater-than-wavelength scale to the subwavelength scale, and as a result, the LMI-EFRC has fostered a world-leading capability for fabrication of complex three-dimensional photonic nanostructures and light absorbers.

Objectives

- Design an optical system for full spectrum photon conversion via optically independent multijunction solar converter architectures to greatly enhance the efficiency of photovoltaic energy conversion.
- Define the limits of absorption and spontaneous emission in optical 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 that 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.

Selected Accomplishments to Date

- Developed flexible concentrator photovoltaics based on microscale crystalline silicon solar cells embedded in downshifting luminescent waveguides, increasing power output by greater than 300%.
- Discovered that to maximize photovoltaic conversion efficiency, photon emission from the solar cell should be maximized. Theoretical results led to Alta Devices' world record 27.6% efficient flat plate single-junction GaAs solar cell in 2011 (now 28.8% in 2012), exceeding the previous record by 2%.
- Developed high quality silver nanoparticle and indium tin oxide inks for direct ink writing of conductive microelectrodes, transparent planar microgrids, and three-dimensional structures.
- Synthesized ordered silicon microwire arrays for photovoltaics that achieve up to 95% peak absorption and up to 85% absorption of day-integrated, above-bandgap direct sunlight.
- Demonstrated the first optoelectronically active photonic crystal light-emitting diode in an epitaxial, single-crystal GaAs photonic crystal with light-emitting heterostructures.

Center Research Team and Scientific Organization

The faculty involved in the LMI-EFRC span 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:

RG-1 Full Spectrum Photon Conversion: Designing photonic materials and structures with controlled optical properties for efficient conversion of the entire solar spectrum via up-conversion, down-conversion, down-shifting, and spectrum splitting.

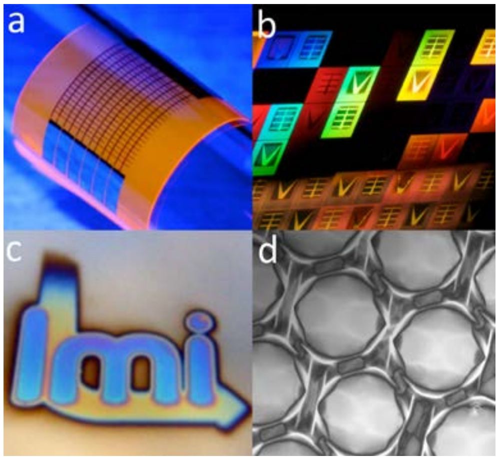

Figure 1. Representative LMI-EFRC research efforts: **(a)** down-shifting luminescent concentrator with micro solar cells, **(b)** large-area nanostructured plasmonic solar cells in amorphous silicon, **(c)** refractive index design via porous etching of silicon, **(d)** three-dimensional GaAs photonic crystal light emitting diode.

RG-2 Optics for Spontaneous Emission and Absorption Enhancement: Investigating dielectric, metallic, and semiconductor light-trapping structures for enhancing absorption in photovoltaics and emission in light-emitting devices. Initial work from RG-2 has identified new optical designs for light trapping beyond the ray optical limit, using both scattering structures and also by exploiting internal photon recycling via spontaneous emission (Figure 2).

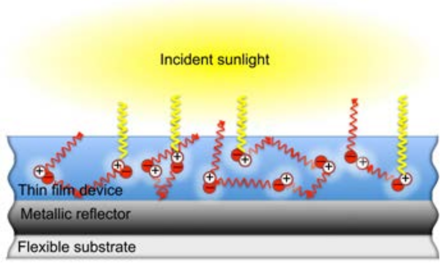

Figure 2. Illustration of photon recycling in a thin film solar cell. This concept discovered by RG-2 researchers motivated the design of Alta Devices' world record solar cell.

RG-3 Transformation Optics for Photovoltaics: Implementing 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.

RG-4 Complex Architecture and Self-Architected Absorbers: Developing photonic structures with preferential morphological and physical orientation of nanostructures on the macroscale for photovoltaic absorption. Complex semiconductor structures such as photonic crystals and silicon microwire arrays give rise to unusual optical properties not found in conventional bulk or thin film solar absorbers. Additionally, we are investigating light-driven synthesis of materials, using light as a tool to control the spatial scale for ordering in complex absorbers.

Light-Material Interactions in Energy Conversion (LMI-EFRC)	
California Institute of Technology	**Harry Atwater (Director)**, Nate Lewis, Austin Minnich
Lawrence Berkeley National Laboratory	Paul Alivisatos, Eli Yablonovitch, Xiang Zhang
University of Illinois, Urbana-Champaign	Paul Braun, Ralph Nuzzo, John Rogers
Harvard University	Jennifer Lewis

Contact: Carrie Hofmann, LMI-EFRC Assistant Director, carrie.hofmann@caltech.edu
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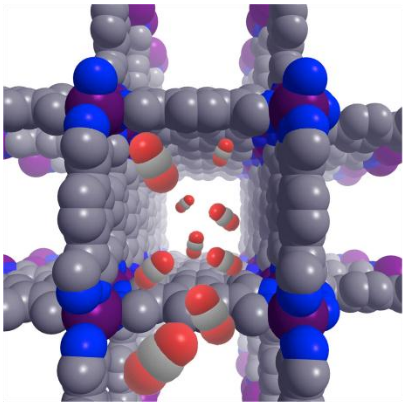
Center for Gas Separations Relevant to Clean Energy Technologies (CGS)

EFRC Director: Berend Smit

Lead Institution: University of California, Berkeley

***Mission Statement**: To develop new strategies and materials that allow for energy efficient gas separations based on molecule-specific chemical interactions, with a focus on carbon capture.*

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 will focus 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 nanoscience to tailor materials that have exactly the right adsorption and diffusion selectivity to enable an economic separations process.

The center brings together personnel with expertise in the following areas of emphasis:

- *Materials Synthesis*: The synthesis of new gas-permeable materials with control over the molecular functionalities to preferentially adsorb gas molecules is essential. Our focus here will be on: (i) generating metal-organic frameworks exhibiting high internal surface areas (up to 4,800 m^2/g) and surfaces lined with robust and tailorable chemical groups and (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	
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Lawrence Berkeley National Laboratory	Maciej Haranczyk, Brett Helms, Jeffrey Kortright, Jeffrey Neaton, Frantisek Svec, Simon Teat, and Omar Yaghi
Texas A&M	Hong Cai Zhou
University of California, Davis	Giullia Galli
University of Minnesota	Laura Gagliardi
National Energy Technology Laboratory	David Luebke

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Molecularly Engineered Energy Materials (MEEM)
EFRC Director: Vidvuds Ozolins
Lead Institution: University of California, Los Angeles

***Mission Statement**: To acquire fundamental understanding and control of nanoscale materials for solar energy generation and electrical energy storage*.

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. MEEM will apply the center's unifying concept of controlling nanometer-scale architectures for achieving unprecedented device performance and manufacturing scalability to two research thrusts: solar energy generation and electrochemical energy storage. We expect to generate molecular design rules for production of optimized nanometer-scale architectures for high performing OPV devices and supercapacitors.

In solar energy conversion, organic photovoltaics (OPVs) offer unique and commercially attractive benefits of lower cost and large-area solution based processing. However, the performance of the most efficient OPV, Bulk Hetero Junction (BHJ) devices, suffers from unreliable synthesis techniques that heavily depend on processing kinetics. Polymer thin-film processing kinetics do not scale well from the laboratory to manufacturing settings, hence, there is a significant need for the rational design of materials that will form robust OPV architectures no matter how they are processed. MEEM will develop the ability to design molecules and architectures for OPV applications in an integrated effort spanning length scales from molecules to complete devices. The center effort involves a combination of self-assembly and molecular recognition with theory, synthesis, and characterization. Our aim is to gain a physical understanding of the architectures and molecular properties that control performance in OPVs, and to develop methods to robustly control those properties using molecular self-assembly. The goal is to engineer devices from the molecules up, optimizing structure and function through routes that will ultimately be better and more reliable than processing kinetics.

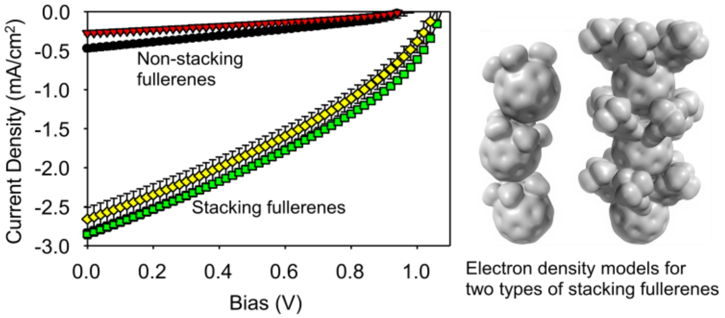

Figure 1. So-called "shuttlecock" molecules based on the heterofullerene $C_{59}N$ with phenyl "feathers" optimized for ideal close contacts within stacks. These molecules self-assemble into one-dimensional wires (right), enhancing the efficiency of charge separation and carrier transport in organic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

Highlights of our progress include demonstration of unique beneficial photophysical behaviors of OPV devices that directly results from designed molecular architecture via self-assembly: nm-scale amphiphilic polymer/fullerene co-assembilies. Our center's work in new fullerenes capable of molecular recognition also yielded a new ***design rule for fullerene acceptors: the optimal nanostructure for fullerene acceptors is an electrically connected linear structure**.* The polymer self-assembly approach is a unique element of our center. Our future OPV efforts are focused on translating these assembly motifs into novel, robust, and high performing OPV device structures.

In energy storage, supercapacitors based on inexpensive metal oxides present an attractive option for large-scale storage from intermittent sources, such as wind and solar, but their widespread adoption is hampered by efficiencies that are significantly lower than theoretical estimates. Our hypothesis is that inefficient charge transport in bulk insulating materials is a crucial bottleneck. MEEM will apply our expertise in understanding and controlling nanometer-scale architectures to elucidate the microscopic factors that limit the performance of oxide-based electrochemical supercapacitors. 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 to capacitively store charge and explore the efficiency of these storage mechanisms in nanoporous materials using both theoretical and experimental approaches.

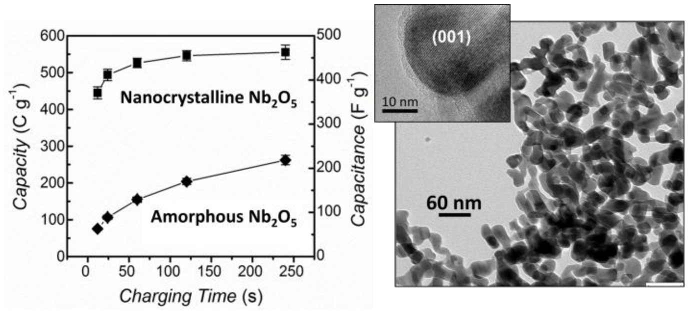

Figure 2: Electrochemical capacitors made from Nb_2O_5 nanocrystals yield significantly faster lithium ion charging kinetics compare to the amorphous form of the mesoporous film.

A notable achievement of our electrochemical supercapacitor team includes the discovery of fast lithium-ion charging kinetics in nanocrystal Nb_2O_5 capacitors, which yielded the highest capacitance observed with Nb_2O_5, at approximately 370 F/g in 12 seconds. The work also produces a ***design rule for Nb_2O_5 and mesoporous film based supercapacitors: presence of an ordered structure is important to achieve high capacity for the insertion reaction***. Additionally, an 3D numerical tool was developed and validated for predicting the capacitances of electric double layer capacitors (EDLCs), offering scaling laws for capacitance-voltage (CV) measurements in EDLCs, providing additional ***design rules for an optimum electrode architecture for ion transport***.

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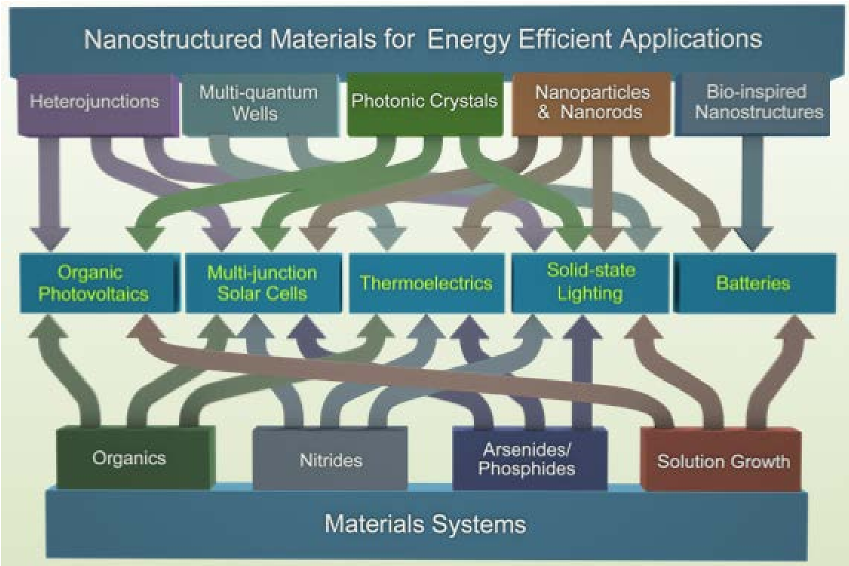
Center for Energy Efficient Materials (CEEM)
EFRC Director: John E. Bowers
Lead Institution: University of California, Santa Barbara

***Mission Statement**: To discover and develop materials that control the interactions among light, electricity, and heat at the nanoscale for improved solar energy conversion, solid-state lighting, and conversion of 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), Purdue University, the National Renewable Energy Laboratory, and the Los Alamos National Laboratory. CEEM's core strength is the unique capabilities of UCSB and its partner institutions to control, synthesize, characterize, and apply materials at the nanoscale for more efficient sustainable energy resources. This expertise is a central theme that unites all the work of the Center and drives the synergy among the various task groups, as illustrated by the accompanying figure. 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.



Organic Photovoltaics: As an overarching goal, the CEEM OPV group seeks to understand conjugated polymer and small molecule semiconductor blends that function as the active layer in solar cell devices. The effort brings together a cohesive and mutually complementary set of experts at UCSB, NREL and LANL to understand what may appear at first sight to be unrelated phenomena. Indeed, the collective CEEM OPV effort very recently led to the design, processing, structural characterization, theoretical understanding and device integration of new types of organic semiconductors, including well-defined molecules that exhibit record power conversion efficiencies.

High Efficiency Multijunction Photovoltaics: Our focus is on novel approaches to InGaN and multijunction photovoltaics for unprecedented high photovoltaic energy conversion efficiencies. This goal requires development of new techniques for the efficient simultaneous coupling of electrons and photons through the various junctions. One of the goals of the project is to develop a five-junction solar cell using a high-bandgap InGaN top junction in combination with a fully lattice-matched underlying arsenide-phosphide four-junction cell. This work requires that we develop new techniques to address the complex issue of designing and fabricating a multi-junction cell in which the optical, electrical, and mechanical properties of each junction are compatible and optimized to provide the highest possible overall efficiency.

Novel Nanostructured Thermoelectrics: Our Scientific objective is to develop new thermoelectric materials whose properties enable us to simultaneously increase the Seebeck coefficient and electrical conductivity, and reduce the electronic and lattice thermal conductivities. We explore a wide range of materials, including 1) semiconductors with nanocrystalline metallic inclusions, 2) new nitride thermoelectric semiconductor materials, 3) electrically conducting crystalline oxides, 4) fine ordered, patterned crystalline silicon nanowire arrays and 5) nanostructured chemical compounds and composites. This involves understanding and engineering the inclusion, transport and scattering of mobile charge carriers and the propagation and scattering of heat-carrying lattice vibrations in the materials, all of which are crucially dependent on the physical and electronic structure of the materials.

High-Power Batteries: Our goal is to develop and apply a new biologically inspired, low cost, low temperature approach to make nanocomposites with exceptionally high power and stability as anodes and cathodes for lithium ion batteries. In addition to the near-term application of the results of these studies for the improvement of batteries and related energy technologies, the broader impact of this research includes a deeper fundamental understanding of the factors governing the control of synthesis, assembly and performance of a wide range of semiconductors and other valuable inorganic materials, to enable their more economical and more efficient use for energy technologies including energy harvesting, transduction and storage.

Solid-state Lighting: Our goal is to advance the fundamental science and technology to both understand factors that limit efficiencies for light emitting diode-based lighting and to provide innovative and viable solutions to current roadblocks. We intend to achieve these goals by: (1) control and elucidation of the carrier loss mechanisms on nonpolar/semipolar GaN LEDs; (2) growth of defect-free bulk GaN crystals; and (3) full-spectrum lighting using an all semiconductor-based emission region; (4) grow devices on nonpolar or semipolar planes to avoid the detrimental effects of polarization-induced electric fields in multiquantum wells arising from discontinuities in spontaneous and piezoelectric polarization at heterointerfaces; and (5) develop and apply photonic crystals to enhance the extraction of light from LEDs.

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
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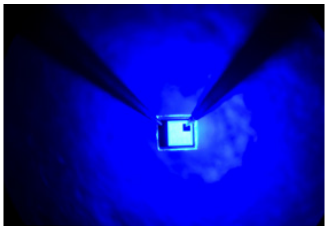

Center for Energy Frontier Research in Extreme Environments (EFree)
EFRC Director: Ho-kwang Mao
Lead Institution: Carnegie Institution of Washington

Mission Statement: *To accelerate the discovery and creation of energy-relevant materials using extreme pressures and temperatures.*

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. In the pressure dimension, creation of novel materials and observation of novel phenomena become the rule rather than exception. The extreme *P-T* studies provide a new route towards discovering advanced structural materials and new materials with enhanced performance for energy transformation (*i.e.* solar, mechanical, chemical to electrical), energy storage (*i.e.*, batteries, capacitors, hydrogen), and energy transmission, sensing and monitoring.

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 critical technologies at national facilities and the 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 organic and inorganic materials and the creation of new electronic and magnetic materials of great significance to energy science. Pressure strongly effects emergent properties as well as ordinary electro-magnetic materials, including high-temperature superconductivity, topological insulators, charge- and orbital-density waves, electronic phase separation, magneto-capacitance, multi-ferroics, spintronics, Mott insulators, 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 in light emission, catalysis, filtering, membranes, etc. and potentially impact 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, T. Strobel, 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

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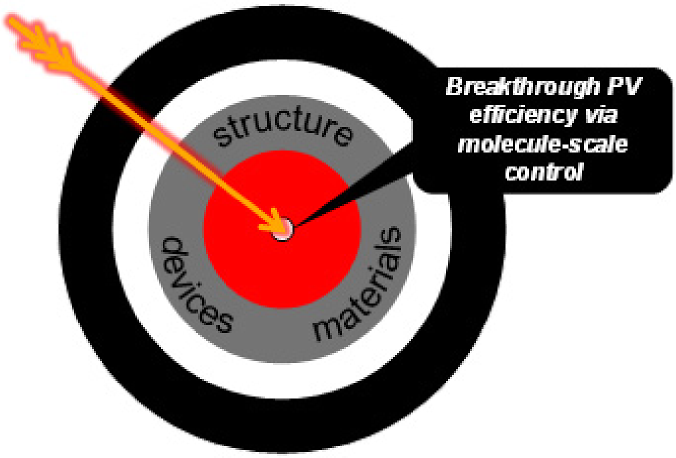
Re-Defining Photovoltaic Efficiency Through Molecule Scale Control (RPEMSC)
EFRC Director: James Yardley
Lead Institution: Columbia University

***Mission Statement**: To develop the enabling science needed to realize breakthroughs in the efficient conversion of sunlight into electricity in nanometer sized thin films.*



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 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 are playing a key role in enabling the development highly-efficient solar energy technologies. The research program of the EFRC centers around four multi-disciplinary and interlocking research thrusts. Each thrust represents an integrated effort incorporating theory, materials, and measurement.

Thrust 1 examines aspects of “Charge Transport Fundamentals in Layered Systems.” In this thrust we are exploring new materials suitable for examination of the fundamental physics in solar cell devices building upon expertise in growing and fabricating structures based on ordered molecular layers one molecule thick including conductors (graphene), semiconductors (molybdenum sulfide) and insulators (hexagonal boron nitride). We are developing methodology for the study of charge creation, dissociation, diffusion, and charge separation in specifically-fabricated layered structures. These materials offer opportunity for fundamental understanding, but also have practical implications. Thus we are examining the efficacy of these new carbon-based conductor materials including graphene for use as transparent conducting materials for efficient extraction of charge from thin film photovoltaic devices. For example we have demonstrated a functioning novel “transparent” solar cell prototypical structure using transparent graphene electrodes for both cathode and anode.

Thrust 2 explores “Multiple Carrier Generation.” Our program is working to identify clear experimental signatures for multi-exciton generation (MEG) processes which are capable of producing multiple pairs of charge carriers with a single photon absorption event. This involves systematic exploration of MEG and related phenomena in quantum dot and carbon-based systems such as graphene nano-ribbons 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. We are examining entirely new mechanisms for the fission of a single excited state into two excited triplet state molecules, which in turn generate two hole-electron charge pairs. This program will allow us to establish a quantitative and predictive understanding for a number of 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.

Thrust 3 is dedicated to “New Materials for Solar Energy.” In this thrust we are developing entirely new, and chemically well-characterized, nanoscale materials. These include new quantum dots materials and novel chemical compounds that we call “molecular clusters.” In addition we have discovered a new class of charge-transfer molecular crystals that open up new solar energy opportunities. 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 these new and novel materials with other semiconductors as well as with metals. Based 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 4 represents a cross-cutting research platform which integrates concepts developed within the EFRC program into solar cell device prototype structures for quantitative demonstration of the efficacy of the technological developments within the Center. We are examining a concept called UTOP (Ultra-Thin Organic Photovoltaics) which is designed to achieve high photo conversion efficiency in very thin organic layers using new optical trapping techniques to efficiently absorb solar radiation. We are exploring prototypical solar cell structures built from unique molecules containing inorganic moieties useful for absorption of solar radiation and generation of excited electron-hole pairs. We hypothesize that these molecular analogs of quantum dots can effectively generate excitons in configurations where exciton transport, charge separation, and charge collection will be highly efficient. We are also actively characterizing prototype structures incorporating graphene electrodes.

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, Ronald Breslow, Luis Campos, Dirk Englund, George Flynn, Irving Herman, James Hone, Laura Kaufman, Philip Kim, Ioannis Kymissis, Colin Nuckolls, Richard Osgood, Jonathan Owen, Abhay Pasupathy, David Reichman, Kenneth Shepard, Michael Steigerwald, Latha Venkataraman, Chee Wei Wong, Xiaoyang Zhu
Purdue University	Ashraf Alam
Brookhaven National Laboratories	Charles Black, Mark Hybertsen, Matt Sfeir

Contact: James T. Yardley
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Energy Materials Center at Cornell (emc ^{2})
EFRC Director: Héctor D. Abruña
Lead Institution: Cornell University

Mission Statement: *To advance the science of energy conversion and storage by understanding and exploiting fundamental properties of active materials and their interfaces.*

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.

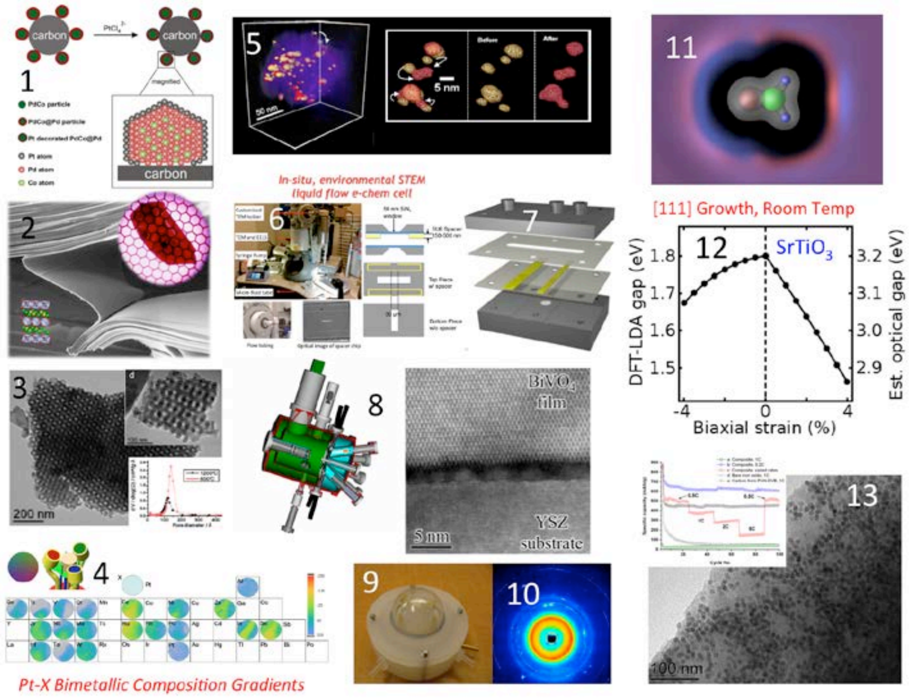

Figure 1

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 materials and nanostructures as catalysts and catalyst supports for fuel cell applications (Fig. 1: 1,2,3,4), their ageing dynamics with atomic resolution (Fig. 1: 5), synthesis and characterization of battery materials (Fig. 1: 13), the synthesis and characterization (with atomic precision and resolution) of core/shell catalysts (Fig. 1: 1) and complex oxides (Fig.1: 8), in-situ characterization via x-rays (Fig. 1: 9,10), development of novel experimental techniques (Fig.1: 5,6,7,9) along with combinatorial high throughput methods (Fig. 1: 4) and screening as well as computational studies (Fig. 1: 11,12).

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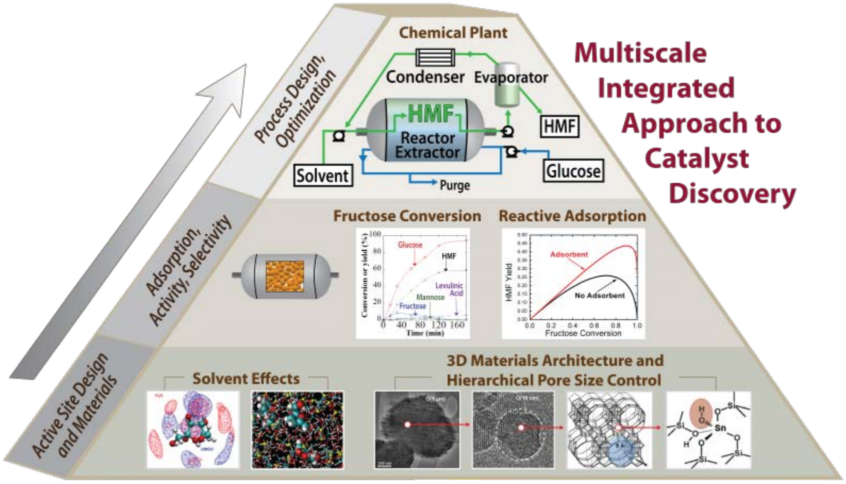
Catalysis Center for Energy Innovation (CCEI)
EFRC Director: Dion Vlachos
Lead Institution: University of Delaware

Mission Statement*: To design and characterize novel catalysts for the efficient conversion of the complex molecules comprising biomass into chemicals and fuels.*

The Catalysis Center for Energy Innovation (CCEI) focuses on developing innovative, science-based heterogeneous catalytic technologies for transformation of lignocellulosic (non-food-based) biomass materials into fuels and chemicals. 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, we must overcome major scientific hurdles that are present due to the inherent complexity of biomass materials and associated processes.

The overall objectives of CCEI are to develop the enabling technologies for biomass conversion that lead to viable, economic operation of future biorefineries and to educate the workforce needed to further develop and implement these new technologies.

Since biomass feedstocks vary considerably by 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. Reactions typically take place in a complex, multiscale environment that renders the rational design of these processes and catalysts very challenging. Our overarching goal is to develop methods and concepts that form the foundations of modern biorefineries. The cornerstone of the CCEI lies in advancing catalysis and its integration into processes that deliver innovative technologies for the conversion of feedstocks of cellulose and hemi-cellulose, sugars (produced from the hydrolysis of biomass), and smaller oxygenated molecules. We have assembled an interdisciplinary team of faculty and scientific staff that brings together the necessary expertise and synergism to tackle the challenges of the complex problems in heterogeneous catalysis.



We exploit various complementary catalytic technological platforms that are anticipated to play key roles in future biorefineries for energy, fuels, and chemical production: (1) novel pyrolysis methods to produce bio-oil, (2) bio-oil upgrade via hydrodeoxygenation, and (3) liquid-phase processing to selectively produce chemicals, such as aromatics.

We have organized the following three crosscutting enablers as the backbone of the center's research to address the inherent complexities of the environment in which reactions take place: (1) hierarchical multiscale materials, (2) multiscale modeling, and (3) characterization. These enablers are integrated within all research thrusts to quickly advance scientific breakthroughs. We develop multiscale models to understand the chemistry and to design new materials. We synthesize hierarchical multiscale materials that are hydrothermally stable, possess tunable porosity with bio-inspired functionality grafted active sites, and minimize molecular traffic-resistance while allowing shape selectivity. Furthermore, we design cutting-edge characterization methods to probe reactions, often under an in situ environment. Research at the Brookhaven National Laboratories is central for in situ characterization of the CCEI catalysts.

The CCEI outcomes 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), Stavros Caratzoulas, Weihua Deng, Douglas J. Doren, Raul F. Lobo, Vladimiros Nikolakis, Stanley I. Sandler, Donald Watson, Bingjun Xu
University of Pennsylvania	Raymond J. Gorte, John M. Vohs
University of Massachusetts	Paul J. Dauenhauer, Wei Fan
University of Minnesota	Aditya Bhan, Michael Tsapatsis, Prodromos Daoutidis
Lehigh University	Mark A. Snyder
Brookhaven National Laboratory	Anatoly I. Frenkel
California Institute of Technology	Mark E. Davis
Columbia University	Jingguang G. Chen
Georgia Tech	Christopher Jones
Massachusetts Institute of Technology	Yuriy Román
Rutgers University	Marianthi Ierapetritou
Pacific Northwest National Laboratory	Ayman Karim

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Center for Advanced Biofuel Systems (CABS)
EFRC Director: Jan Jaworski
Lead Institution: Donald Danforth Plant Science Center

Mission Statement: *To generate the fundamental knowledge required to increase the efficiency of photosynthesis and production of energy-rich molecules in plants.*

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, and Jaworski 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.

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, 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, Terry Woodford-Thomas, Jim Umen
Michigan State University	Yair Schachar-Hill, Christoph Benning
University of Missouri – St. Louis	Sam Wang
New Mexico Consortium/Los Alamos National Laboratory	Richard Sayre
University of North Caroline at Chapel Hill	Leslie Hicks
Washington State University	David Gang
University of Nebraska	Edgar Cahoon

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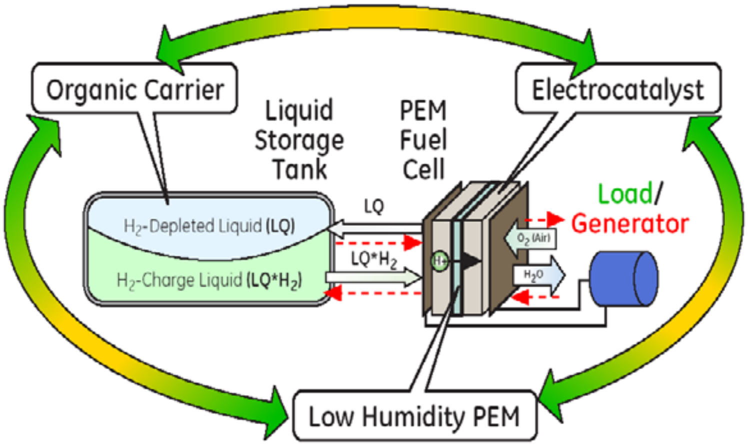
Center for Electrocatalysis, Transport Phenomena, and Materials (CETM) for Innovative Energy Storage
EFRC Director: Grigorii Soloveichik
Lead Institution: General Electric Global Research

Mission Statement: *To 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, 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 common 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.



CETM has identified three major research challenges in electrocatalysis, transport phenomena in membranes, and material compatibility to make this concept a reality. The selection of organic carriers suitable for organic fuel cell/flow battery is based on thermodynamic and kinetic factors central to hydrogenation and reversible dehydrogenation reaction mechanisms and is 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 two protons and two electrons per unsaturated C=X bond. Because only a few examples of catalysts for electrohydrogenation and electrodehydrogenation of organic heterocycles are known, promising leads from among the following classes of catalyst are being explored: i) catalysts for activation of the C-H bonds, ii) catalysts for hydrogenation of imines and carbonyl bonds, iii) catalysts for hydrogenation of arenes, particularly heteroarenes, and iv) catalysts that can reduce water to H_2. The emphasis will be made on non-precious metal complexes and materials.

Various strategies are being 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 is studied to identify any limitations placed on the electrodehydrogenation and electrohydrogenation activities.

To develop a novel low-humidity 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. The following major problems are being investigated: effect of the organic carriers on proton transport and membrane morphology, replacement of water with other proton conductive phase, and effect of polymer structure on membrane properties.

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

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, P. Bonitatibus, M. Doherty, L. Krishnan, 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

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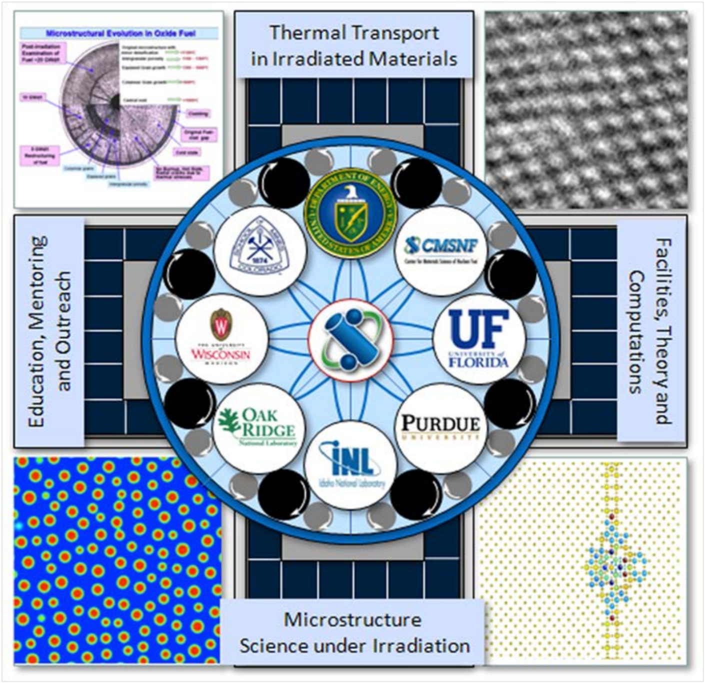
Center for Materials Science of Nuclear Fuel (CMSNF)
EFRC Director: Todd Allen
Lead Institution: Idaho National Laboratory

***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.*

Research Direction: The Center will enrich the scientific basis of thermal transport in the ceramic materials (UO_2) used as nuclear fuel, based on an understanding of phonon transport through the unique microstructures formed under radiation at high temperature. Although there is significant interaction among the group members across both research areas, the objectives can be broadly classified as thermal transport and microstructure science under irradiation.

The research objective of the ***thermal transport thrust*** area is to develop a computational model for thermal transport in irradiated materials with complex defect structures. This thrust area will also conduct measurements of lattice dynamics and conductivity targeting the impact of defects on thermal transport.

The research objective of the ***microstructure science under irradiation thrust*** area is to develop predictive capabilities for defects and microstructure evolution in irradiated fuels and to conduct irradiation and microstructure characterization experiments to understand defect and microstructure processes in UO_2 and surrogate systems.



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 stated objectives are ultimate goals for the Center and are the basis for an ambitious long-term research program. Within this context, the Center is answering a subset of key scientific questions, which will form a foundation for attaining these broader objectives. These scientific questions are:

- **Thermal Transport**
  - How do anharmonicity, fission product impurities, and chemical stoichiometry impact phonon lifetimes and thermal transport as a function of temperature in single crystal UO_2?
  - How do microstructural features such as grain boundaries, dislocations, interfaces, voids and bubbles affect thermal transport in UO_2 before and after irradiation?

- **Microstructure under Radiation**
  - What type of clusters are produced by irradiation of UO_2 what do we need to understand the energies and kinetic paths of formation of clusters in UO_2, and predict atomic scale mechanisms of nucleation in UO_2?
  - What is the impact of temperature and oxygen environment on the stoichiometry of single and polycrystalline UO_2 before and after irradiation?
  - How do dislocation loops and gas bubbles form and grow in irradiated UO_2?

The Center brings together an internationally renowned, multi-institutional team of (1) experimentalists at Idaho National Laboratory, Oak Ridge National Laboratory, Colorado School of Mines, University of Florida, and University of Wisconsin, and (2) computational materials theorists at Idaho National Laboratory, University of Florida, and Purdue University to focus on understanding microstructure science under irradiation and its effects on thermal transport.

The framework of nonlinear dynamics of irradiation-driven materials will lead to an atomistically-informed generalized mesoscale phase-field model for the irradiation-induced microstructure evolution, which will furnish the defect state impacting thermal transport. This approach will capitalize on the team's demonstrated strength in theoretical and computational modeling of materials at all scales. In close synergy with the modeling effort, the experimental team will perform advanced microstructure and thermal-transport studies on ceramic fuel materials using an array of state-of-the-art characterization techniques. They will also use the unique experimental capabilities of U.S. Department of Energy (DOE) user facilities, including the Advanced Test Reactor, Spallation Neutron Source, High Flux Isotope Reactor, Intermediate Voltage Electron Microscope, and Advanced Photon Source.

Center for Materials Science of Nuclear Fuel (CMSNF)	
Idaho National Laboratory	**Todd Allen (Director),** David Hurley, Jian Gan, Xianming Bai, Marat Khafizov, Jianguo Yu
Purdue University	Anter El-Azab
University of Florida	Michele Manuel, Simon Phillpot
University of Wisconsin	James Blanchard
Oak Ridge National Laboratory	Ben Larson, Judy Pang

Contact: Todd Allen, Scientific Director, ATR National Scientific User Facility, Idaho National Laboratory
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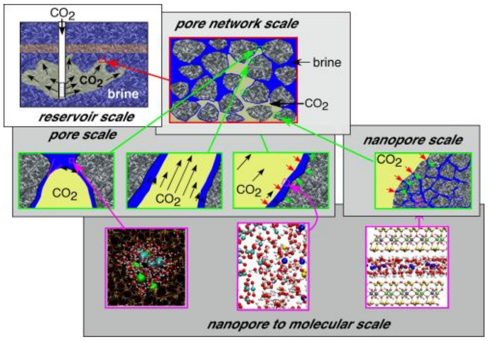
Center for Nanoscale Control of Geologic CO_2 (NCGC)

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

Mission Statement: *To build a fundamental understanding of molecular-to-pore-scale processes in fluid-rock systems, and to demonstrate the ability to control critical aspects of flow, transport, and mineralization in porous rock media as applied to the injection and storage of carbon dioxide (CO_2) in subsurface reservoirs.*



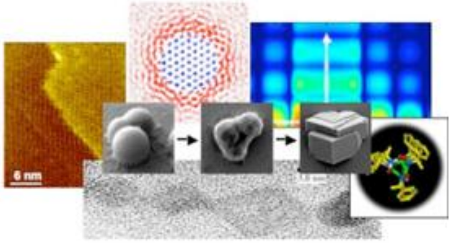
Technical Overview: The vision for the Center is to understand, predict, and enhance the performance of underground CO_2 storage systems. Specific goals are to (1) establish novel molecular, nanoscale, and pore-network scale approaches for controlling flow, dissolution, and precipitation in deep subsurface rock formations to achieve 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 the fate of injected CO_2 that is applicable for a 1000 years into the future. Our focus is at the nano- to pore scale where subsurface processes originate from chemical and physical interactions. The word "control" in the title has a double meaning – it connotes an effort to better understand how nanoscale processes control larger scale processes, and, more heroically, to use such information to optimize storage of injected CO_2.

The NCGC consists of a team of highly qualified investigators with expertise in, and access to, the most advanced analytical and computing facilities available for furthering fundamental knowledge of the nanoscale properties and processes of CO_2-brine-mineral systems. Our primary objective is not to provide specific engineering parameters for a subsurface storage system, but to raise understanding of fluid-rock processes to a new level using a coordinated and focused research effort. Although we expect the new knowledge we generate to be useful for applications other than CO_2 storage, the unique character of the NCGC derives from its focus on supercritical CO_2 and its behavior and fate in subsurface reservoirs, and the scale and coordination of the research effort.

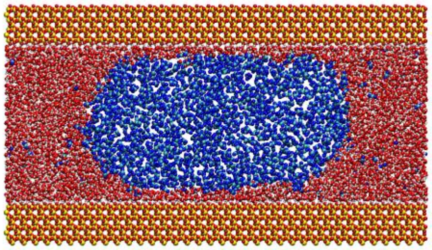
The NCGC is focused on three aspects of geologic carbon sequestration:

1. Understand and enhance mineralization of injected CO_2
2. Optimize the performance of geologic traps and seals
3. Understand and optimize reservoir fluid-rock reactive transport processes

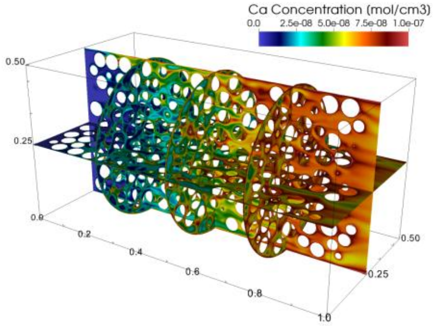
Our largest effort (Thrust Area 1) is on understanding how carbonate minerals nucleate and precipitate under the conditions of CO_2 sequestration in both reservoir rocks (e.g. sandstones) and geologic seals (shales). This emphasis follows from the fact that in many reservoir rocks, there is sufficient cation supply to mineralize most of the CO_2, but the release rate of cations by dissolution is slow and hence the long-term system performance is uncertain. Thrust 1 also capitalizes on the rapid progress being made on molecular scale understanding of mineral dissolution and precipitation processes stimulated by the tools available at the DOE light sources, computing centers, and nanoscience and technology centers. The remainder of the NCGC effort (Thrust Areas 2 and 3) is focused on the properties of fluid mixtures under confinement in high-surface area environments, and the interplay between flow and chemical reactions; the latter involves understanding the geometrical relationships between CO_2, brine, and minerals, and the mechanisms by which mineral fluid-reactions are affected by the unique features of the two-phase (or 3-phase) fluid system. Thrusts 2 and 3 include key computational research tasks, and unique opportunities afforded by the neutron facilities at ORNL. The nanoscale processes involved in CO_2 sequestration are first aggregated at the pore scale (µm to mm). Thrust Area 3 is focused on pore scale and multi-scale heterogeneity effects on CO_2 trapping.



Mineral-fluid reactivity: Thrust Area 1 aims to provide an understanding of the molecular scale mechanisms and materials parameters that govern the processes of dissolution and precipitation under reservoir conditions, with the ultimate goal of establishing the upscaled parameters that will enable accurate modeling of reservoir- wide evolution, and the scientific basis for engineering approaches to enhancing CO_2 trapping processes.



Nanopore Processes: Thrust Area 2 focuses on properties of confined fluids, a key issue relevant to the behavior of caprocks and the reactivity of reservoir rocks. A related issue is the wetting properties of minerals, which arise from molecular-scale properties of fluid-fluid and fluid-solid interfaces and is essential to predicting the capillary pressure curves of reservoir rocks and caprocks, properties that strongly influence the efficiency of reservoirs and the security of caprocks. Wetting contrasts also produce thin films on minerals, which vary with changes in mineralogy, pore water chemistry, or other conditions, and strongly affect the long-term distribution and reactivity of CO_2.



Pore-Scale Processes: Thrust Area 3 investigates "emergent processes" associated with the injection of CO_2 into the deep subsurface, which forces the subsurface system far from equilibrium, where a range of self-organizing processes can lead to emergent, time-dependent structures. Our focus is on structures that emerge due to process coupling at the pore scale, since this is ultimately the framework within which the fluids migrate and/or reside and minerals dissolve and precipitate. This research is bringing to bear a new generation of experimental, imaging and modeling tools specifically designed to address pore scale dynamics.

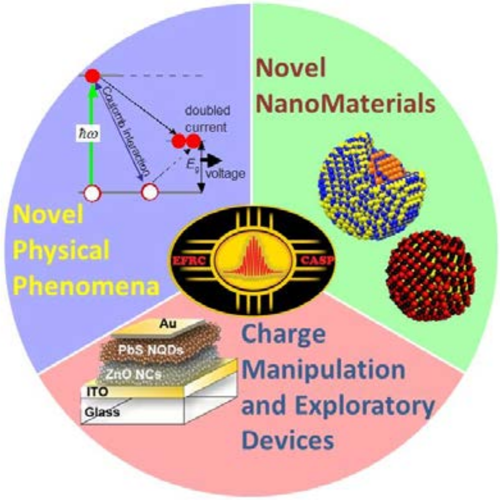
Center for Nanoscale Control of Geologic CO_2	
Lawrence Berkeley National Laboratory	D.DePaolo (Director), C. Steefel (Deputy Director, Theme Lead), J. Ajo-Franklin (Theme Lead), I. Bourg (Theme Lead), Participants: C. Ajo-Franklin, Y. Kim, S. Pride, G. Sposito, T. Tokunaga, D. Trebotich, J. Urban, G. Waychunas, J. Wan, S. Whitelam, L. Yang, R. Zuckerman
University of California, Berkeley	Technical Lead: J. Banfield
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
Pacific Northwest National Laboratory	Technical Lead: J. DeYoreo
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, 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: *To capitalize on recent advances in the science of how nanoparticles interact with light to design highly efficient materials for the conversion of sunlight into electricity.*

Technical Overview: Breakthroughs in solar energy conversion cannot be expected to come 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, particularly in the form of quantum-confined semiconductor nanostructures, are expected to offer new processes that could yield progress toward this goal.



The research of this Center concentrates in three main Thrust areas of exploration:

- *Novel nanoscale physical phenomena for efficient capture and conversion of light into electrical charges;*
- *New means for efficient charge manipulation and transport in nanoassemblies, and proof-of-principle device structures that exploit emergent nanoscale physics;*
- *Novel engineered nanomaterials for controlling and exploiting novel physical phenomena, and for applications in exploratory devices.*

The Novel Physical Phenomena (NPP) Thrust. The new physical phenomena for light harvesting and conversion into electrical charges that are explored in the NPP Thrust involve carrier multiplication (generation of multiple excitons by a single absorbed photon), 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 hybrid nanostructures can be used to extend the range of excitonic transfer, and tune the strength of carrier-carrier Coulomb coupling.

The Charge Manipulation and Exploratory Device (CMD) Thrust. Effective exploitation of the unique properties of nanostructured materials in solar energy conversion, especially in utilizing multiple excitons, is contingent upon our ability to efficiently extract and transport carriers to charge collecting electrodes. To this end, the CMD Thrust explores charge separation and transport, as well as energy transfer, in engineered nanoassemblies. Specific research topics include extraction of multiple charges, and the mechanism of charge or exciton transport in extended nanocrystal arrays. 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 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.

The Novel NanoMaterials (NNM) Thrust. 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 NNM 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 and create unique functionalities in new engineered semiconductor nanocrystals and hybrid composite nanomaterials. Three main areas of research within this Thrust include developing high quality solution-processible NCs of solar-relevant 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, K. Velizhanin
National Renewable Energy Laboratory	M.C. Beard (Associate Director), J.C. Johnson, J.M. Luther, N.R. Neale
University of California, Irvine	M. Law
University of Minnesota	U. Kortshagen
University of Colorado	D.M. Jonas, A.J. Nozik
Colorado School of Mines	P.C. Taylor
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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 interactions of defects at interfaces in materials subjected to extreme radiation doses and mechanical stress in order to synthesize new interface-dominated 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: (i) *How do we design and perfect atom and energy-efficient syntheses of revolutionary new forms of matter with tailored properties*?, and (ii) *How do we characterize and control matter away-especially very far away-from equilibrium*? In responding to these grand challenges our center focuses on designing structural nanomaterials for tailored response 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 interface-dominated materials where the atomic structures of the interfaces are used to tailor the interactions of point and line defects with interfaces and hence, the macroscopic material properties.

We have developed a set of common scientific issues that 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; and 3) Interface-driven mechanical response. We attempt to address these issues through a hypothesis-driven R&D approach that integrates experiments and theory. The key deliverables from this research program will be quantitative relationships between the atomic structure and energetics of interfaces and radiation or mechanical damage evolution in materials. These quantitative relations are *figures-of-merit* that can be used to rank different solid-solid interfaces in terms of the ability of an interface to control defect evolution.

Our center has two thrust areas in *irradiation extremes* and *mechanical extremes* respectively. The irradiation extremes thrust studies a range of radiation damage phenomena relevant to fusion and fission energy over a broad range of metal-metal, metal-oxide and oxide-oxide interfaces. The mechanical extremes thrust explores severe plastic deformation processing such as accumulative roll bonding (ARB) to design nanocomposites with interfaces that are crystallographically and morphologically stable at large plastic strains. The behavior of these ARB-processed nanocomposites is explored in a variety of conditions such as shock, high-pressure torsion, irradiation, fatigue, etc. Besides ARB, physical vapor deposition is used to synthesize model bi-layer or multi-layer systems for ion irradiation studies. Given the focus on mechanistic understanding at the level of atomic structure of interfaces, we study model systems such as Cu-Nb, Cu-Ag, $SrTiO_3$-TiO_2, etc where accurate interatomic potentials are available so that experimental results can be integrated with theory. For other more complex systems such as metal-oxide (Fe-Y_2O_3, Fe-TiO_2, etc) efforts are underway to develop charge-transfer based interatomic potentials. Likewise for long-time-scale simulation defect cluster evolution, method development activities involve atomistically-informed kinetic Monte Carlo approaches.

The progress in the development of *figures-of-merit* for interfaces is summarized in the following table.

Research Goals	Progress in the first 3 years
Understand helium storage at interfaces.	▪ Developed an equation that correlates the concentration of stored helium (He) at interfaces with the interface structure. ▪ Developed an equation-of-state for He bubbles at interfaces. ▪ Demonstrated suppression of material hardening due to He bubbles at interfaces. ▪ Collectively, the new understanding gained and the predictive capability that results will provide design principles for structural materials in fusion energy.
Understand sink efficiency of interfaces for radiation-induced point defects.	▪ Identified the types of point defect interactions at interfaces in terms of interface atomic structure and defect energetics and kinetics. ▪ Developed a model that accounts for the balance between irradiation conditions and recovery processes in nanoporous and multilayer materials.
Understand response of structure-less interfaces to radiation-induced point defects.	▪ Elucidated how point defects redistribute at interfaces in terms of defect energetics and kinetics. These results are being integrated into a predictive model that will enable the design of materials for fission energy applications.
Understand evolution of stable interfaces under severe plastic deformation.	▪ Discovered stable interfaces under accumulative roll bonding and developed theory for crystallographic and chemical stability of interfaces. Predictive capabilities are being developed.
Understand dislocation or twin nucleation at interfaces.	▪ Discovered deformation twin nucleation from specific interfaces in bulk accumulative roll bonding nano-composites. ▪ Identified how the interface structure affects defect (glide dislocation or deformation twin) nucleation at the interface. ▪ Initiated a predictive model, based on these results, which will provide the design principles for processing bulk nanocomposites for structural and nuclear energy applications.
Understand shock response of interfaces.	▪ Discovered varying shock response (e.g., stable or migrating boundaries, transgranular or intergranular spall) as a function of boundary structure. These results are being integrated into a predictive model that will enable the design of materials with a tailored response in high strain rate applications.

Center for Materials at Irradiation and Mechanical Extremes (CMIME)	
Los Alamos National Laboratory	A. Misra (Director), I.J. Beyerlein (Co-Director), Senior Personnel: B.P. Uberuaga, N. A. Mara, O. Anderoglu, J.A. Caro, J. Carpenter, E.K. Cerreta, S. Choudhury, S. J. Fensin, G.T. Gray, Q. Jia, N. Li, S.A. Maloy, E. Martinez-Seaz, J. Mayeur, S.M. Valone, A.F. Voter
Carnegie Mellon University	Senior Personnel: A.D. Rollett
University of Illinois, Urbana Champaign	Senior Personnel: R.S. Averback, P. Bellon
Massachusetts Institute of Technology	Senior Personnel: M. J. Demkowicz
University of Nebraska, Lincoln	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**: To build effective catalysts from first principles via computational catalysis and atomic-level characterization.*

***Rationale**.* Recent advances in computational catalysis, synthesis of solid catalytic surfaces at the nanoscale, and in our ability to unambiguously characterize these materials, may allow us to control and direct energy-related reactions in ways not now possible. Despite rapid progress in these areas, we do not yet have the ability (a) to computationally design an ideal catalyst for a reaction of reasonable complexity at conditions of practical interest, (b) to prepare the catalyst with a degree of atomic-level precision that mimics the surfaces that we can simulate by computation, nor (c) to characterize the catalyst surface with atomic-level resolution, especially at working conditions.

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 length scales 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).

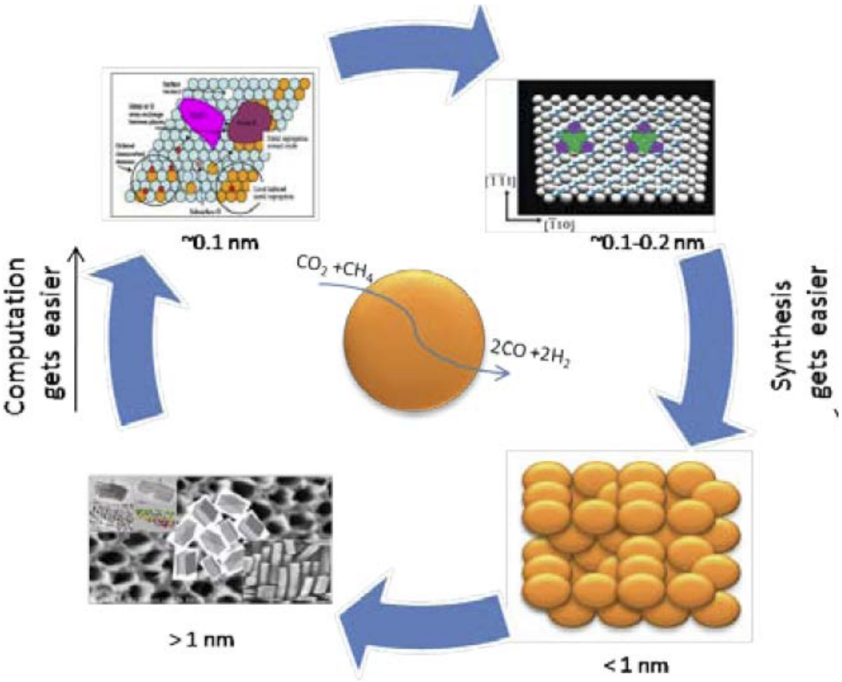

Fig. 1. Schematic representation of the degree of difficulty in computation and synthesis of catalysts.

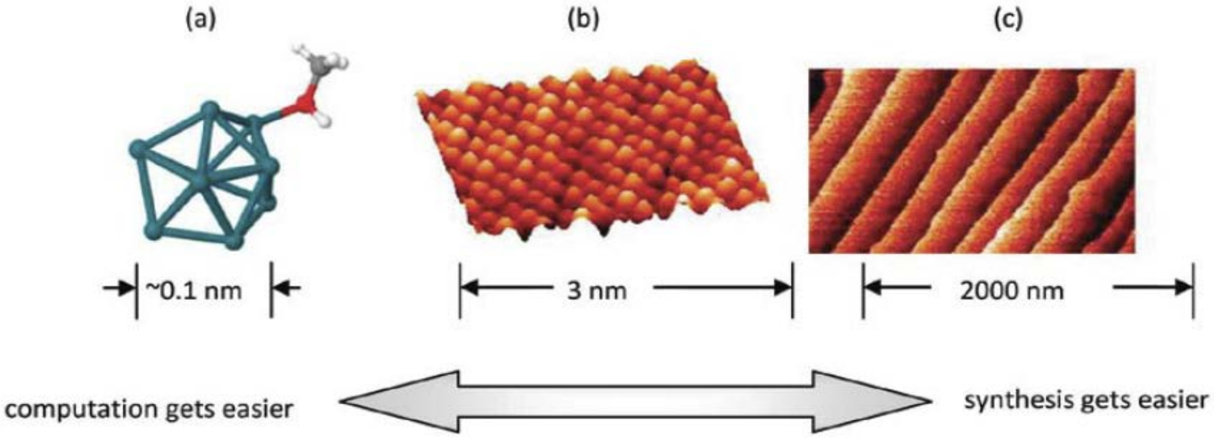

Fig. 2. Difficulty of computational and synthesis/characterization research vary in opposite directions with length scale; (a) CH_3OH on Rh_7 cluster (DFT model by D. Bruce, Clemson Univ.); (b) $Pt_{25}Rh_{75}(100)$ Alloy 3-d topography (www.omicron.de); (c) Mono-atomic steps on SiO_2 layer - in UHV 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 focuses 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 are being explored. Modeling predictions are validated by experiment. While Density Functional Theory (DFT) has been a very useful complement to surface science experiments, our multi-scale modeling is designed to 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 is an iterative one that 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, Y. Xu
Clemson University	D. Bruce
Texas A&M University	L. Liu
Georgia Tech	D. Sholl
University of Utrecht, Netherlands	K. P. de Jong, P.E. de Jongh
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Grambling State University	N. Seetala

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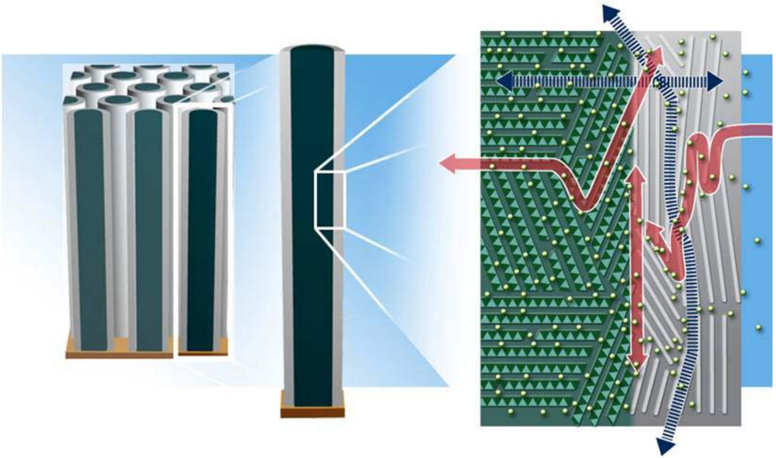
Nanostructures for Electrical Energy Storage (NEES)
EFRC Director: Gary W. Rubloff
Lead Institution: University of Maryland

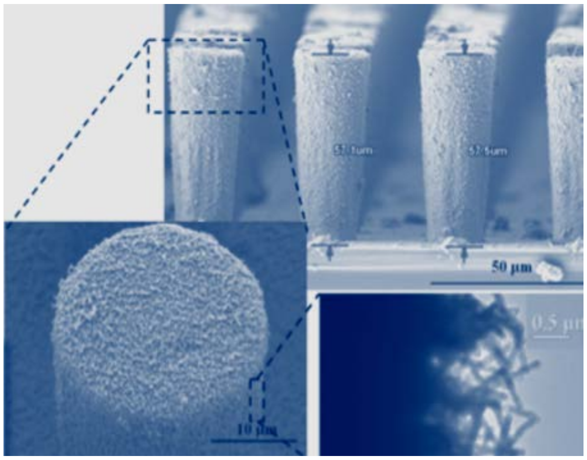
Mission Statement: *To understand and build nanostructured electrode components as the foundation for new electrical energy storage technologies*

The NEES Energy Frontier Research Center takes on fundamental challenges in lithium-ion battery and supercapacitor energy storage by investigating systems at the length scale of one to hundreds of nanometers. The members of NEES synthesize and study precisely made nanoparticles, nanotubes, nanowires, and nanometer-thick films of different materials (i.e. “nanostructures”). We focus on how the geometry and structure of those materials and configurations of the nanostructures together affects their properties.


The schematic of nanostructured heterogeneous electrode shows the separate ion storage and electron transport layers.

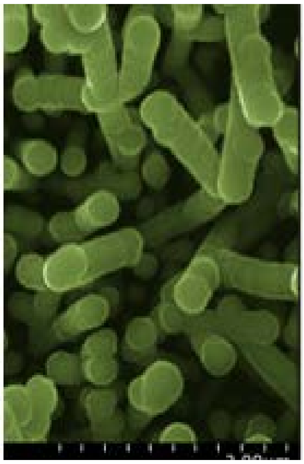
The Center’s vision holds that heterogeneous combinations of oxides, silicon, and novel forms of carbon in nanostructures promise to meet the multifunctional requirements of high power, high capacity electrodes. By specifically examining nanostructures that are composed of well-defined and closely controlled materials and geometries, the Center has ideal platforms for investigating how lithium-ion conductivity and capacity, electrical conductivity, and mechanical stability limit the lifetime, energy density, and power of electrochemical energy storage.

NEES has four strategic directions. In the **Cathodic Nanostructures** and **Anodic Nanostructures** strategic directions, researchers explore the underlying processes that control the behavior of carbon nanotubes, graphene, and other carbon materials that are combined with either an oxide material or silicon. The carbon materials in pristine form are both mechanically strong and excellent electronic conductors, while nanoscale oxides and silicon store and release high densities of lithium ions at high rates. Combining the expertise of electrochemists, materials scientists, electrical engineers, and physicists, the Center’s effort analyzes fundamental issues in nanostructure synthesis, charge transport kinetics, and mechanical stability during cycling.



The **Enabling Science & Methods** strategic direction develops model nanostructured systems and creates new instruments and techniques to probe their properties. Researchers create experimental and computational models of surface and interface evolution, critical for teasing out the core factors at play at the junctions of heterogeneous materials.

The researchers also develop new measurement techniques, including microsystems for use in-situ high-resolution transmission electron microscopy (TEM) to evaluate nanoscale processes during electrochemical reactions. They have also developed novel cantilever structures to measure structural changes at the nanoscale. The microsystems for in-situ electrochemical TEM are being developed as a Discovery Platform at the Center for Integrated Nanotechnologies, a user facility that is a joint venture between Sandia National Laboratories and Los Alamos National Laboratory, and thus the platform will be available to the wider scientific community.



The fourth strategic direction on **Nanostructure Forests** is a new area of NEES investigation. Building off the knowledge gained from studying individual nanostructures, researchers investigate ion flow around and to large numbers of nanowire electrodes. The transport of charge through a 'forest' of nanowires presents intriguing challenges for understanding the influence of nanopore geometries and high surface areas on electrolyte flow.

Nanostructures for Electrical Energy Storage (NEES)	
University of Maryland	G.W. Rubloff (Director), S.B. Lee, J. Cumings, R. Ghodssi, Liangbing Hu, J. Reutt-Robey, C.S. Wang, Y.H. Wang
Sandia National Laboratories	C.T. Harris, S. Hearne, K. Jungjohann, K. Leung, J.P. Sullivan, A. Talin, K. Zavadil
University of California - Irvine	R.M. Penner, P.G. Collins, Z. Siwy
Los Alamos National Laboratory	J. Yoo
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Center for Excitonics (CE)
EFRC Director: Marc Baldo
Lead Institution: Massachusetts Institute of Technology

***Mission Statement**: To understand the transport of charge carriers in synthetic disordered systems, which hold promise as new materials for conversion of solar energy to electricity and electrical energy storage.*

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) Coherence and disorder

The aim of this working group is to understand exciton transport in locally organized materials. Our first model system is photosynthetic antennas. Photosynthesis is an excitonic system that has been optimized for more than 2 billion years. What can it tell us that is fundamental about controlling the transport of excitons? Our second model system is J-aggregates, where we perform theory and experiments. J-aggregates are self-assembled semicrystalline structures that are relevant to practical organic solar cell materials. Here, the key questions are: What controls exciton formation in these structures? How big are the excitons? Do they spread out over multiple molecules? And what is the role of disorder? In both model systems, we also address the role of coherence. One of the most exciting research directions at present is the suggestion that phase coherence in the initial life of the exciton might help its transport within photosynthetic structures. We are pursuing this direction with the development of a 2D Fourier Transform Spectroscopy tool with a unique ability to quickly reconfigure multiple beams using a spatial light modulator.

(ii) Semiconductor Nanocrystals

Semiconductor nanocrystals are the perfect example of energy localized into excitons by material design. In this group, we seek to understand exciton dynamics in semiconductor nanocrystals using multiexciton spectroscopy and photonic interrogation of single quantum dots in the visible and infrared. Two key fundamental problems are addressed in studies of single quantum dots. First, what is the origin of 'blinking'? This is the phenomenon where a single dot mysteriously and transiently turns off, and is no longer able to emit light. Is it still observed in the infrared? Second, what is the efficiency of multiple exciton generation in the infrared? By generating more than one charge per incident photon, this process could increase solar efficiencies beyond the single junction limit. Interrogating individual nanocrystals is a challenging task due to the inherently small optical cross section. We are pursuing two approaches to this problem. First, we are developing superconducting nanowire single photon detectors (SNSPDs). Second, we are building photonic nanostructures to collect photons for single nanocrystals. To complete our efforts, we are examining the dynamics of quantum dot films in electroluminescent structures. What are the efficiency losses in these devices? How can they be operated at very high brightness?

(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 working group combines excitons with photons to form 'exciton polaritons' - new states of matter and energy. The combination of excitons and photons has important new properties that may be exploited in new classes of energy conversion devices, especially ultralow threshold lasers that may be the foundation of future solid state lighting.

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, K.A. Nelson, B. Olsen, T.M. Swager, H. Tuller, T. Van Voorhis
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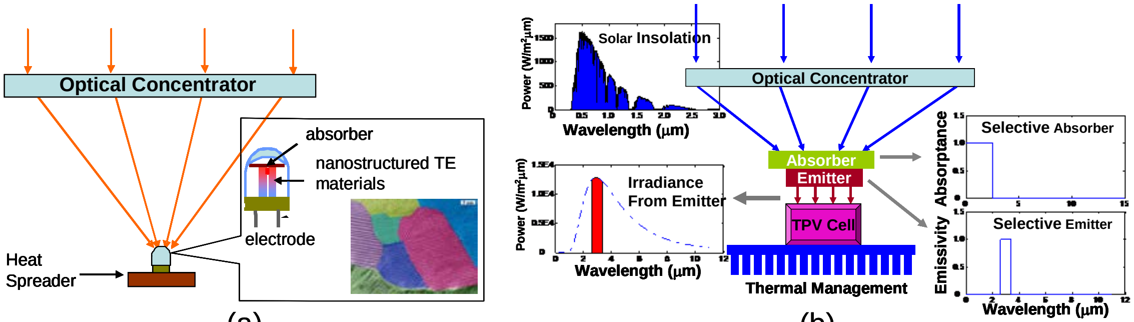
Solid-State Solar-Thermal Energy Conversion Center (S^{3}TEC Center)
EFRC Director: Gang Chen
Lead Institution: Massachusetts Institute of Technology

***Mission Statement**: To create novel, solid-state materials for the conversion of sunlight into electricity using thermal and photovoltaic processes.*

The S^{3}TEC 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^{3}TEC center aims at advancing thermoelectric materials through detailed experimental and theoretical studies of electron and phonon transport in nanostructures and bulk materials. Optical pump-probe and neutron scattering will be used to understand phonon transport, together with quantum and classical simulation of phonon transport in bulk and nanostructured materials. Electron spectroscopy will be performed in both thermoelectric materials and at the electrical contact regions, together with transport modeling. Both thin films and bulk nanostructures will be investigated, aiming at eventual large scale applications. Proof-of-principle prototypes will be built to demonstrate the concepts and the potential of the solar thermoelectric generation. Neutron spectrometers and STEM at Oak Ridge National Laboratory will be used for phonon spectroscopy and



(a) (b)

Figure 1 Solid-state solar-thermal energy conversion technologies to be pursued at the S^{3}TEC 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.

high-resolution imaging of interfacial structures. Fundamental studies will be conducted to understand high temperature stability of nanostructured materials, and interfacial transport between electrodes and thermoelectric 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. Other novel concepts taking advantages of the high-temperature photonic spectral control are also being exploited.

The S^3TEC 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^3TEC Center)	
Massachusetts Institute of Technology	**G. Chen (Director)**, **E.N. Wang, (Associate Director)**, M.S. Dresselhaus, E.A. Fitzgerald, P. Jarillo-Herrero, J. Joannopoulos, S.-G. Kim, K. A. Nelson, Y. Shao-Horn, and C.A. Schuh, M. Soljacic
Boston College	D. Broido and C.P. Opeil
Oak Ridge National Laboratory	O. Delaire and D.J. Singh
University of Houston	Z.F. Ren
Rensselaer Polytechnic Institute (seed funding)	T. Borca-Tasciuc and G. Ramanath

Contact: Gang Chen
Carl Richard Soderberg Professor of Power Engineering
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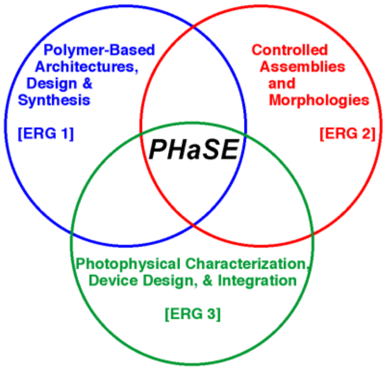
Polymer-Based Materials for Harvesting Solar Energy (PHaSE)
EFRC Directors: Thomas P. Russell and Paul M. Lahti
Lead Institution: University of Massachusetts Amherst

Mission Statement: *To carry out fundamental photovoltaic-oriented research on the use of 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.*

Center Research Portfolio:

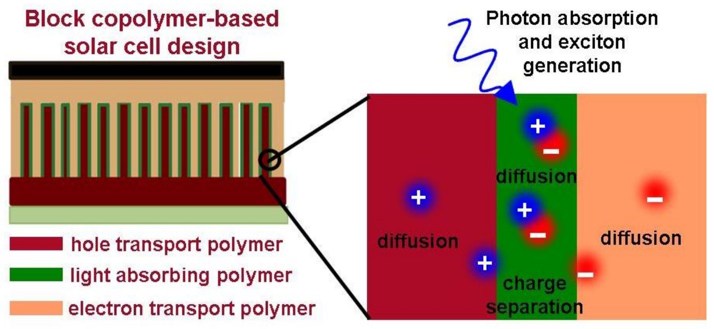
The University of Massachusetts EFRC integrates investigators from multiple departments and institutions into three distinct but interlinked Energy Research Groups or ERGs: ERG 1 *Polymer Based Architecture: Design and Synthesis*, ERG 2 *Controlled Assemblies and Morphologies*, ERG 3 *Photophysical Characterization, 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 Laboratory 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 The Pennsylvania State University. Inorganic nanoparticle/nanorod synthesis and assembly at UMass Amherst is enhanced by collaborations at the World Premier Institute, Advanced Institute of Materials Research at Tohoku University.



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 new p-type and n-type semiconductor polymers for light harvesting and photocurrent generation that can be used as active electronic layers in solar cells. Synthetic strategies focus on molecular self-assembly for morphological control, with structure-tunable photophysical characteristics that assist charge movement in a polymer solar cell. A unifying objective of all work is to provide a range of polymer and nanocomposite materials for assembly and behavior testing in ERGs 2 and 3.

ERG 2. The design and fabrication of a high-efficiency photovoltaic (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, theory, and engineering of polymers; all work together to devise means to control self-assembly and morphology of individual polymer chains in thin films. A major ERG 2 centered focus is the development of general strategies of polymer and molecular nano-scale assembly that work for a range of promising electronic materials. This will allow faster comparisons of efficacy for new materials, using the same assembly and testing process. This strategy also is being used to control morphology and structure of polymer-based and polymer/inorganic-based hybrid materials to optimize PV efficiency. The lessons gained from these studies can then be applied in test device fabrication.

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 charges across organic-electrode interfaces (see figure). All of these processes must be understood to design higher efficiency solar cells. Causes of detrimental effects – like charge carrier recombination and trapping – need to be assessed to avoid structures or morphologies that lead to them. State-of-the-art optical and microscopy techniques are being developed and utilized to study lifetimes and mechanisms of these processes.



Schematic of 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 photovoltaic composite films composed of polymers and molecules assembled on the nano-scale by methods developed in ERG 1 and ERG 2. Single-molecule and time-resolved spectroscopies provide valuable mechanistic insight about the electronic effects of synthetic building block variation and assembly on the fundamental processes in PV systems. A “feedback loop” of design ✩ synthesis-assembly ✩ physical process evaluation ✩ test device evaluation allows identification of the most promising materials and strategies for more rigorous charge mobility test and photovoltaic device fabrication in PHaSE's Photovoltaic & Optical Spectroscopy Facility, and in collaboration with UMass Lowell and Penn State. Computational modeling of these processes, including collaborative work at RPI and Oak Ridge, is also important to predict which materials and assembly schemes are most effective.

Polymer-Based Materials for Harvesting Solar Energy	
University of Massachusetts Amherst	*Directors*: T. P. Russell, P. M. Lahti *Senior Personnel* (*ERG Coordinators*): M. D. Barnes, T. S. Emrick, D. Maroudas, D. Venkataraman *Senior Personnel*: A. Briseno, E. B. Coughlin, A. Crosby, A. Dinsmore, V. Duzhko, G. Grason, R. Hayward, 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. E. Mallouk
University of Massachusetts Lowell	*Senior Personnel* (*subcontract site lead investigator):* J. Kumar
Oak Ridge National Laboratory	*Senior Personnel* (*major collaborator*): B. Sumpter
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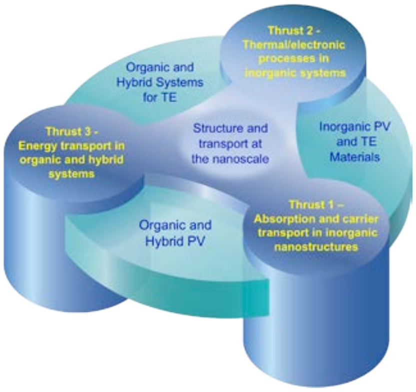
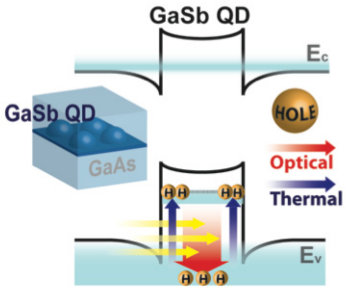
Center for Solar and Thermal Energy Conversion (CSTEC)
EFRC Director: Peter F. Green
Lead Institution: University of Michigan, Ann Arbor

***Mission Statement**: To study complex material structures on the nanoscale to identify key features for their potential use as materials to convert solar energy and heat to electricity.*

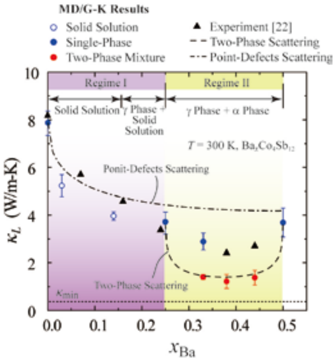
Research in CSTEC falls in three synergistic and collaborative thrusts, under a unifying concept: *structure and transport at the nanoscale.* Energy conversion processes in materials are the result of a complex interplay between structure (which includes aspects of symmetry and dimensionality) over different length scales, while the dynamic processes that occur over a wide range of time scales. The basic challenge is to access the wide range of length and time scales in order to understand and then overcome the trade-offs associated with the complex energy conversion processes involved. Achieving our objectives requires a team with diverse expertise working closely together in a highly collaborative manner on different aspects of the problem.



The objective of the first thrust, **CSTEC Thrust 1**, is to exploit unique quantum effects at the nanoscale to understand and to maximize the absorption of energy from sunlight and to minimize energy losses, associated with carrier transport, using nanostructured inorganic materials, including highly mismatched Alloys (HMAs) and quantum dots, to achieve high efficiency solar energy conversion. We synthesize nanostructured materials architectures for solar energy conversion such that the *optical absorption* and *electronic transport are tailored to achieve* properties not available in the bulk, circumventing, for example the trade-off between absorption and transport efficiency of bulk systems. Specific systems under investigation include the following: (a) **Intermediate band concepts exploiting** nanostructures involving QD: Type-I and II, to control carrier life times and absorption (b) **highly mismatched alloys** (GaAs:N, GaAs:Bi, and ZnTe:O) with tailored band gaps, lattice spacings and densities of states in order to control electron and phonon transport.



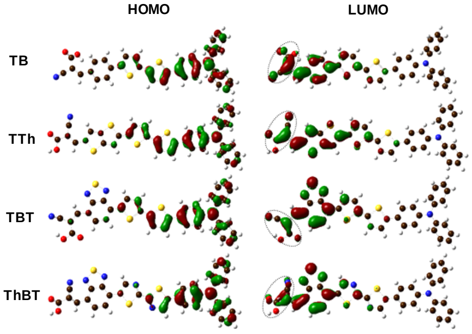
Energy band diagram of a quantum dot with a type II band line-up



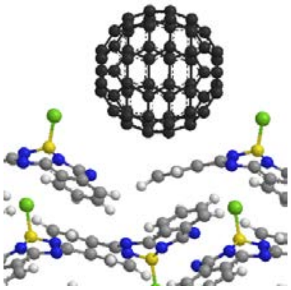
Theoretical predictions of the thermal conductivity in different phases of a skutterudite thermoelectric material

The objective of **CSTEC Thrust 2** is to understand and to exploit fundamental mechanisms and processes associated with electron and hole transport, as well as electron-phonon coupling, in materials, with the goal of achieving high figures of merit in thermoelectric (inorganic, hybrid or molecular) materials. 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 to improve the thermoelectric figure-of-merit.

In **CSTEC Thrust 3** we investigate the molecular and structural origins of energy conversion (absorption, carrier generation and recombination, transport) phenomena in organic and hybrid material systems with the goal of producing highly efficient materials and morphological structures for OPVs. Our efforts to develop and to maximize the performance/efficiency of OPVs include: (1) a combined experimental / computational approach to the molecular design and synthesis of new materials; (2) the design and development of processing strategies to control morphology at the nanoscale; (3) the measurement and prediction of structure and carrier transport, and (4) materials and nanoscale photonics optimization to enhance absorption.



Homo/Lumo levels calculated for molecules synthesized for solar energy conversion



Simulations of molecular configurations in C_{60}/SubPc

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, 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, Akram Boukai, Emmanouil Kioupkis, Jennifer Ogilvie, Jamie Phillips, Pramod Reddy, Katsuyo Thornton, Anton Van Der Ven, Steve Yalisove
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Center for Revolutionary Materials for Solid State Energy Conversion (RMSSEC)

EFRC Director: Donald T. Morelli

Lead Institution: Michigan State University

Mission Statement: *To investigate the underlying physical and chemical principles of advanced materials for the conversion of heat into electricity.*

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. anharmonic solids with low intrinsic thermal conductivity
V. thermoelectric and mechanical characterization of new thermoelectric materials
VI. fundamental scientific issues related to thermoelectric devices and systems

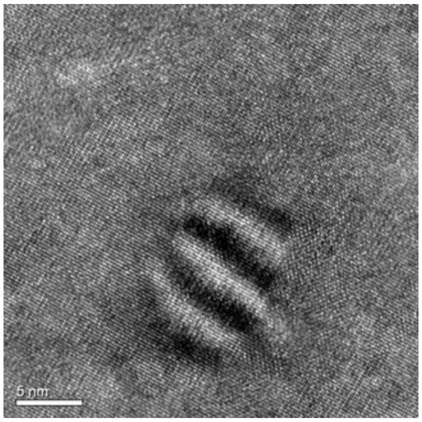

Figure 1 High resolution TEM image showing spinodally decomposed regions in PbTe-16%PbS.

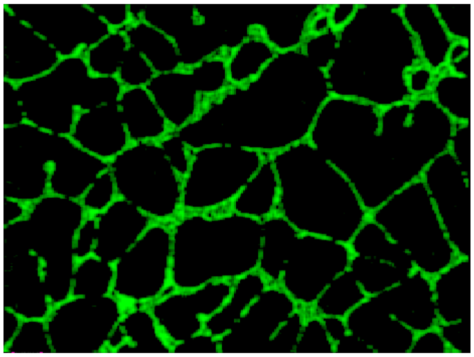

Figure 2 Auger map of boron (green) decorating grain boundaries in a Co-Si alloy.

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**.

Center for Revolutionary Materials for Solid State Energy Conversion (RMSSEC)	
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Center for Inverse Design (CID)
EFRC Director: Bill Tumas
Lead Institution: National Renewable Energy Laboratory

***Mission Statement**: To revolutionize the discovery of new materials by design with tailored properties through the development and application of a novel inverse design approach powered by theory guiding experiment with an initial focus on solar energy conversion.*

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. 1. 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 conductors, we have selected ternary chalcogenides and ternary oxides, 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 a 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., crystalline solids, alloys, nanostructures, molecular structures). Our center is generating general methodologies to be tested on specific cases, but that have future potential to open the door for much broader applications.

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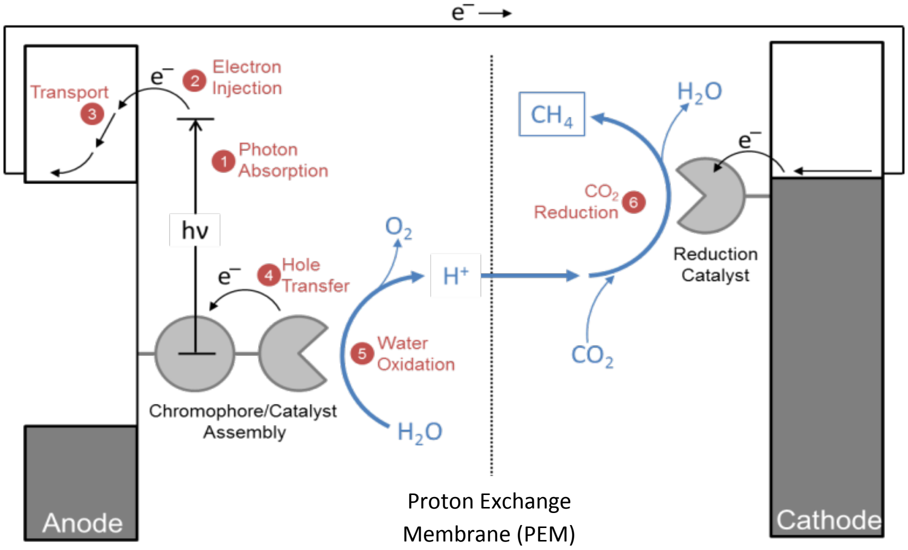
Center for Solar Fuels (UNC)
EFRC Director: Thomas J. Meyer
Lead Institution: University of North Carolina at Chapel Hill

Mission Statement*: To integrate academic and translational research to study light/matter interactions and chemical processes for the efficient production of solar 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 approach is distinctive based on the design and utilization of separate functional modules, maximizing their performance, and integrating them into device prototypes featuring both single and tandem photoelectrode configurations.**

Multiple themes have been developed in parallel ‐ 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 ‐ with integration in photoelectrochemical cell configurations. 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 from, and is enriched by, parallel research in electrocatalysis and Dye Sensitized Solar Cells.

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 provide guiding principles for component design, integrated systems, and devices, and (5) augmentation of research findings and multidisciplinary strengths in research collaborations with national laboratories, other EFRCs, and the Research Triangle Solar Fuels Institute (www.solarfuels.org). The latter has been a key partner, extending the research findings of the EFRC through the translation stage to device prototypes.

TEAM STRUCTURE and RESEARCH FOCUS

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

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 and chromophore-catalyst applications.
	Peptides	Molecular assemblies based on peptide scaffolds for exploitation of antenna effects and chromophore-quencher applications.
	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.
Theory	Theory	Research integrated across the Center on reaction pathways, electron and energy transport, molecular design, systems analysis.

Center for Solar Fuels	
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Duke University	D. Beratan, M. Therien, W. Yang
Georgia Institute of Technology	J. Reynolds
North Carolina Central University	D. Taylor
University of Florida	K. Schanze
Research Triangle Institute	P. Hoertz
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Non-equilibrium Energy Research Center (NERC)
EFRC Director: Bartosz A. Grzybowski
Lead Institution: Northwestern University

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

Our efforts encompass development of far-from-equilibrium statistics, dissipation vs. structure relationships, construction of dissipative/metastable materials (including those with internal feedbacks and those that can self-replicate), and networks of dissipative processes giving rise to complex non-equilibrium systems. From a fundamental point of view, understanding the relationship between dissipation and organization/function of matter out of equilibrium is one of the great challenges facing the physical sciences – in particular, general laws describing dissipative systems would not only allow us to understand better the operation of animate matter (as all organisms are dissipative!) but would also identify the rules/requirements under which artificial materials and systems become least dissipative and, therefore, most energetically efficient. An integral part of NERC's vision is to translate such a theoretical description into the design and synthesis of specific non-equilibrium systems: maximally efficient molecular machines and their collections, materials that convert different forms of energy in the least dissipative fashion, networks of chemical reactions working in synchrony to produce desired products in an optimal fashion, as well as systems that exhibit auto-catalysis, self-organization, and self-replication (each of which requires energy input and dissipation). All in all, our aim is to channel and control dissipation and to put the energy thus "saved" to a useful task.

Since the time of Gibbs, equilibrium has become a familiar and powerful concept. Equilibrium structures, systems, and materials are all governed by the principles of equilibrium thermodynamics and correspond to minima of appropriate thermodynamic potentials. Although finding predictive relationships between the interactions acting in an equilibrium system/material and its final structure might be difficult, it is, at least in principle, possible. This convenient situation changes dramatically in systems displaced from thermodynamic equilibrium – either into kinetically trapped states or into states in which 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 (NE) regime is painfully inadequate. This lack of theoretical understanding limits the development of truly non-equilibrium systems and materials. Such materials are of great interest and promise because it is only outside of thermodynamic equilibrium that one can achieve life-like behaviors such as adaptation, feedback, or self-replication. It is only outside of equilibrium that molecular switches can act as true molecular machines, plasmons can catalyze chemical reactions, and multiple chemical reactions can act in synchrony as chemical systems.

NERC is perhaps the first-ever large-scale collaborative research effort devoted to the study and implementation of non-equilibrium systems and materials. The research team assembled within NERC comprises some of the most accomplished scientists in the world with a unique combination of skills ranging from modeling of non-equilibrium phenomena to the synthesis of molecules and materials that can function outside of equilibrium. The uniqueness of the Center lies in bringing all these diverse skills under one research umbrella and combining them into projects that, in the vast majority of cases, involve both theorists and experimentalists. The success of our effort depends crucially on maintaining the proper collaboration (and also balance!) between theory and experiment and also the balance between the individual creativity of the PIs and the programmatic focus. Since non-equilibrium is a very broad concept and its study could easily become a collection of disjoint research projects on various manifestations of dissipative phenomena, the effort of NERC must be – and is – at all times re-assessed and, if necessary, refocused around the most fundamental and the most practically relevant aspects of energy dissipation. The current focus areas are (i) Theory and Model Systems; (ii) Non-equilibrium Materials; and (iii) Networks.

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.

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 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).

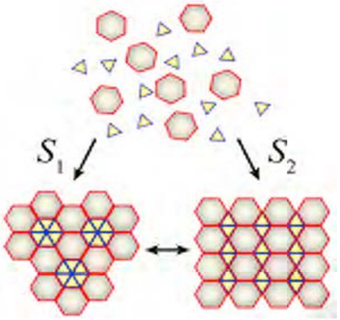

Figure 1. Different stimuli, *S*, evolve the same set of components into different "adaptive" materials.

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)	
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Harvard University	G.M. Whitesides
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Argonne-Northwestern Solar Energy Research (ANSER) Center

EFRC Director: Michael R. Wasielewski

Lead Institution: Northwestern University

Mission Statement: *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 for optimizing solar energy conversion. Achieving integrated artificial photosynthetic systems requires hierarchical organization at both molecular and supramolecular levels to capture light energy, separate charges, and transport them to catalytic sites at which fuel synthesis occurs, e.g., H_2O splitting to generate H_2. Subtask 1 research targets discovering the fundamental scientific principles that are necessary to (i) self-assemble biomimetic molecular systems to harvest light and perform photochemical charge separation, (ii) couple photogenerated charges to multi-electron, multi-metallic catalysts for H_2O oxidation and H^+ reduction to H_2, and (iii) develop bio-inspired supramolecular assemblies for producing tailored nano-environments necessary for an integrated artificial photosynthetic system (e.g. Fig. 1).

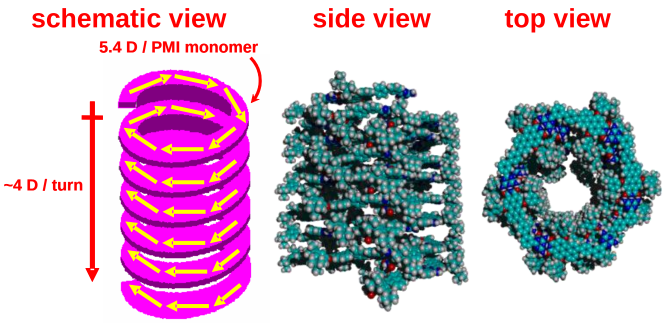

Fig. 1. Self-assembling nano-environment for integrated artificial photosynthesis.

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.

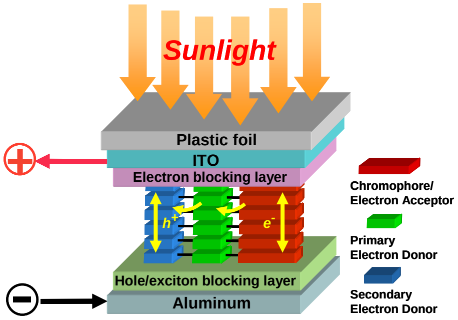

Fig. 2. A multilayer organic solar cell.

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, insulating oxide and metal nanostructures that can be utilized to systematically control key electronic, catalytic, and optical phenomena, as well as to favorably manipulate device dynamics and energetics. The resulting unique structures enable 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).

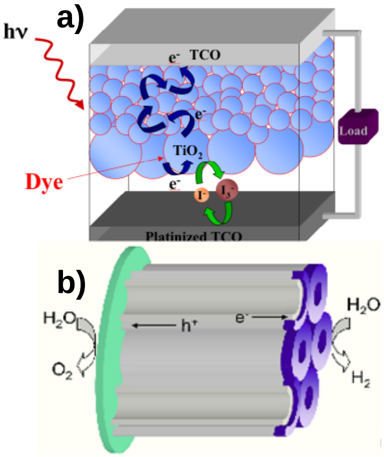

Fig. 3. a) DSSC based on electron injection into a wide bandgap, nanocrystalline, n-type semiconductor. **b)** *Compartmentalized* light-harvesting, catalytic oxidation, and catalytic reduction components function on a high-area, high-porosity, electrically conductive platform.

Argonne-Northwestern Solar Energy Research (ANSER) Center	
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Argonne National Laboratory	L. X. Chen, J. Elam, A. Martinson, M. J. Pellin, O. Poleuktov, D. Tiede, G. Wiederrecht
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Materials Science of Actinides (MSA)
EFRC Director: Peter C. Burns
Lead Institution: University of Notre Dame

Mission Statement*: To understand and control, at the nanoscale, materials that contain actinides (radioactive heavy elements such as uranium and plutonium) to lay the scientific foundation for advanced nuclear energy systems.*

The *Materials Science of Actinides* Center unites researchers from seven universities and two 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.

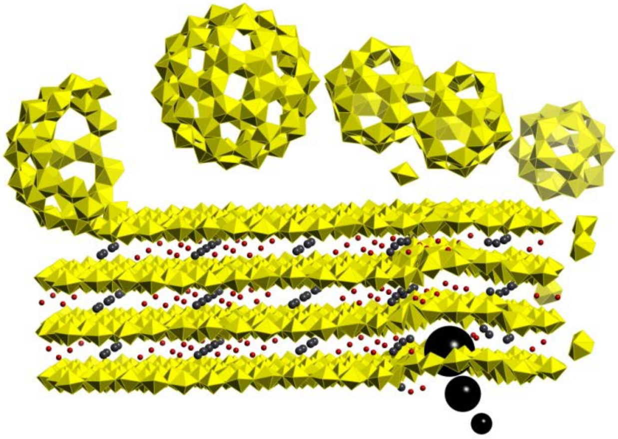
The complex actinide materials theme includes the synthesis and properties of fluorite-structured materials with tetravalent actinides in solid solution, as well as the effects of extreme environments on such materials. It also encompasses the complex structural topologies typical of the higher-valence 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	
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University of California, Davis	A. Navrotsky, W. Casey, M. Asta
George Washington University	C. Cahill
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Oregon State University	M. Nyman
Florida State University	T. Albrecht-Schmitt
Stanford University	R.C. Ewing
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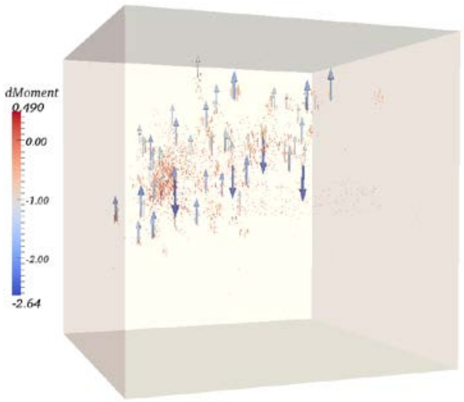
Center for Defect Physics in Structural Materials (CDP)
EFRC Director: G. Malcolm Stocks
Lead Institution: Oak Ridge National Laboratory

Mission Statement: *To enhance our fundamental understanding of the defects, defect interactions, and defect dynamics that determine the performance of structural materials in extreme environments.*

Defects of various types are ubiquitous in structural materials and ultimately control their properties. When materials are exposed to irradiation, the existing defects are altered and new ones created. Consequently, the properties of materials under irradiation continually evolve in response to defect creation, defect annihilation, and resulting changes in microstructure. The *Energy Frontier Center for Defect Physics in Structural Materials (CDP)* is developing an unprecedented level of knowledge about defect physics at the finest temporal and spatial scales in irradiated materials through the development and use of new computational and experimental tools to access these scales. Through a focus on Fe and Fe-based alloys as models of the steels that are the workhorse structural materials for energy, the knowledge derived from CDP activities will provide the requisite foundation to accurately predict how materials respond and perform under irradiation, while simultaneously laying the groundwork to guide and accelerate the development of materials that are resistant to radiation-induced property changes.

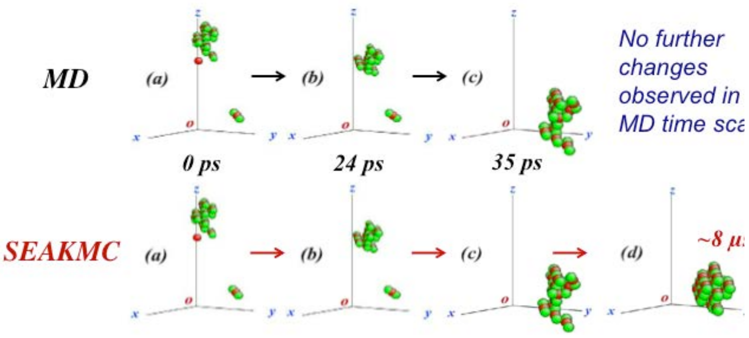
Coarse Graining Approach to Large Scale *Ab Initio (DFT)* Calculations



Changes in local magnetic moments on Fe atoms during a 50KeV radiation damage cascade – 1,024,000 atom supercell: blue (red) moment reduction (enhancement)

The CDP employs a multidisciplinary team that is developing and deploying novel experimental (X-ray, Transmission Electron Microscopy (TEM), Nano-mechanical testing) and theoretical techniques (large scale *ab initio* electronic structure, quantum informed molecular dynamics, atomistic kinetic Monte-Carlo methods) that can jointly probe the production and evolution of irradiation induced defects, their subsequent interaction with dislocations and consequent effect on materials strength. Specifically, the CDP develops approaches that *push the length and timescales of experiment down* and the *length and timescales of theory modeling and simulation up* to a point where they overlap; thereby, allowing the most direct tests of the underlying theoretical models. This approach makes it possible, for the first time, to directly test models and to identify strengths and deficiencies and to develop models that have

Self-Evolving-Atomistic-Kinetic Monte-Carlo



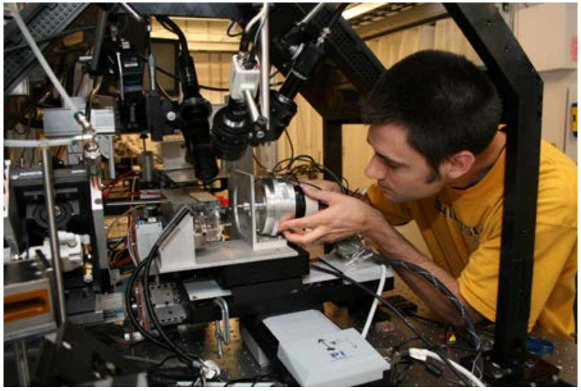
SEAKMC: *A new atomistic approach to modeling defect diffusion/interaction at time scales (10^{-7} – 10^{3} s) inaccessible to Molecular Dynamics (< 10^{-6} s)* been validated at the most basic level of “atoms and electrons”.

Within this overall context the CDP focuses on two interconnected themes:

- *Defect formation and short-term evolution under irradiation*
- *Dislocation interactions with radiation produced defects*

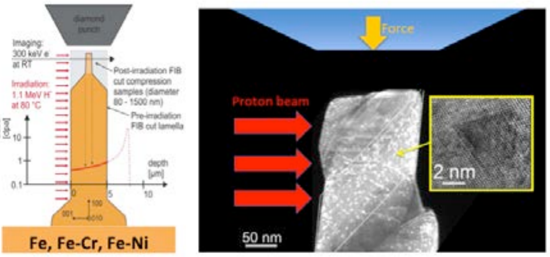
In the first theme, the goal is to obtain a quantitative understanding of the mechanisms of defect formation and short-term defect evolution that determine material behavior and the properties of Fe-based alloys under irradiation. We employ advanced *ab initio* and atomistic methods to determine defect character and properties, and the influence of magnetism and solutes. In addition we directly compare predicted microstructures to experimental results obtained by employing x-ray diffuse scattering and *in situ* TEM. The goal of the second theme is to develop a rigorous understanding of the fundamental unit events that control strength and deformation by studying the interaction of dislocations with both preexisting defects, such as grain boundaries, and the defects produced by irradiation. To accomplish this, the CDP is deploying a suite of new experimental tools that includes: 3D X-ray microscopy, TEM (both high resolution and *in situ* deformation) and *in situ* nano-mechanical testing.

New In Situ 3D X-ray Testing Capability at APS



Sub-micron stress measurement by 3D X-ray

Nano-Mechanical Testing of Irradiated Pillars



Quantitative in situ mechanical testing of irradiated samples during transmission microscopy provides direct information on defect interactions and effects on plastic deformation.

Center for Defect Physics (CDP)	
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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.*

Fluids can be gas-like or liquid-like, and solids can be crystalline or amorphous. The key features of fluid-solid interfaces (FSIs) are the high mobility and often reactivity of the fluid phase, and the structural control provided by the solid phase. Many advanced energy technologies involve FSIs, and FIRST focuses on two critical important interfacial systems, those involved in electrical energy storage (batteries, capacitors) and heterogeneous catalytic systems for conversion of fluid components (*e.g.* water, CO_2) to useful products, like fuels. The overarching goal of the FIRST Energy Frontier Research Center is to address the fundamental gaps in our current understanding of such FSIs, by addressing 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 dense fluids (water, polar organic solvents, room temperature ionic liquids, etc.) with solid substrates controls many chemical processes encountered in nature and industry. However, the atomic-nanoscale structures, reactivities and transport properties at the 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, heterogeneous catalysis, materials synthesis and chemical separations. 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

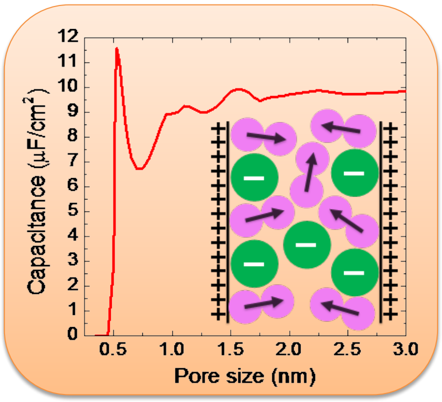

Figure 1. Capacitative behavior of ions in a dipolar solvent at a nanoporous electrode surface (representative of the electrolytes used in batteries and supercapacitors) simulated using Classical Density Functional Theory (Jiang et al., *J. Phys. Chem. Lett.* **2012**, *3*, 1727-1731).

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 (**Figure 1**), surface roughness, functionalization and alteration due to chemical reactions with the fluid influence solvent/solute transport at uniquely-tailored carbon surfaces and with novel electrolyte structures and chemistries. In Thrust 3, we seek to identify the unique properties of interfacial fluids that control reaction pathways, selectivity, and energetics (**Figure 2**) of proton-coupled electron transfer (PCET) in redox couples and in reactions involving H_2O, O_2 and CO_2.

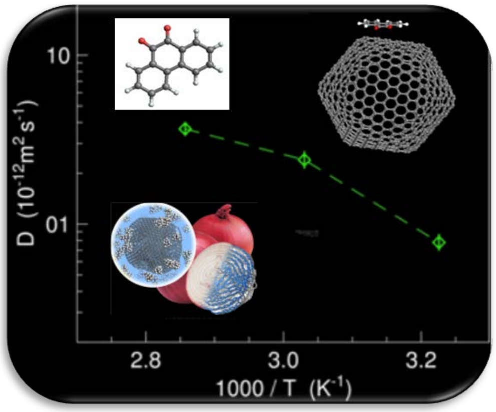

Figure 2. Diffusion of a candidate PCET reactant (9,10-Phenanthrene quinone) on onion-like carbon nanoparticle surfaces determined from quasielastic neutron scattering studies (Chathoth et al., *J. Phys. Chem. B* **2012,** *116*, 7291-7295).

The First Center brings 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. The research is mainly conducted at Oak Ridge National Laboratory (ORNL), with extensive activities at our partner institutions. Much of the key research is conducted through peer-reviewed proposals to major DOE 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 the Advanced Photon Source (APS) at Argonne National Laboratory. The Center currently supports 20 students, postdoctoral fellows and research associates at ORNL and our partner institutions.

Fluid Interface Reactions, Structures and Transport (FIRST) Center	
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Georgia State University	G. Wang
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Pennsylvania State University	A.C.T. van Duin
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Center for Molecular Electrocatalysis (CME)
EFRC Director: R. Morris Bullock
Lead Institution: Pacific Northwest National Laboratory

***Mission Statement**: To understand, design, and develop molecular electrocatalysts for solar fuel production and use.*

Electrocatalysts that efficiently convert electrical energy into chemical bonds in fuels, or the reverse, converting chemical energy to electrical energy, will play a critical 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 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 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 or carboxylic acids) 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 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.*

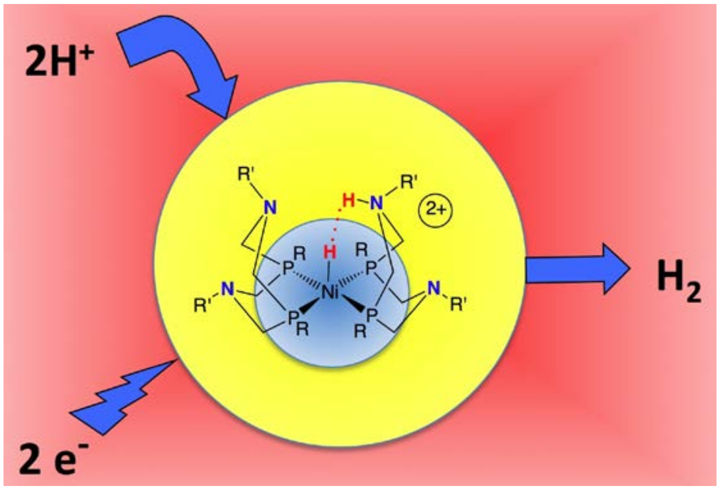
The reduction of protons derived from water to form hydrogen is shown in eq. 1 (forward direction). The reverse process, the oxidation of H_2, is an important reaction in hydrogen fuel cells. The four-electron reduction of O_2 to form water, (eq. 2, forward direction), is important in almost all currently 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 1% or more 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 necessity of fossil fuels to produce the H_2.

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

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

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

Molecular catalysts offer a degree of precise structural control – and therefore the precise probing of relationships between catalyst structure and activity – that are not possible for either heterogeneous catalysts or enzymes. *It is precisely this structure-activity knowledge that we are seeking to develop*. The two-, four-, and six-*electron* redox processes in eqs. 1-3 for H_2, O_2, and N_2, are also two-, four-, and six-*proton* processes. Facile and controlled movement of both electrons *and* protons from solution to



substrates bound at the active metal site is essential for these electrocatalytic reactions. Proton transfers need to be very carefully controlled and designed to obtain optimal rates and efficiency of molecular electrocatalysts. 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 have been shown to play an important role in hydrogenase enzymes, the oxygen-evolving complex, and other biological systems.

Primary goals of the Center for Molecular Electrocatalysis are to:

- Obtain a fundamental understanding of how proton relays accelerate proton transfers, both intra- and *inter*molecularly
- 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	
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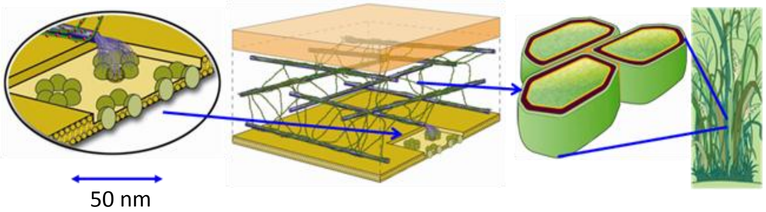
Center for Lignocellulose Structure and Formation (CLSF)
EFRC Director: Daniel Cosgrove
Lead Institution: Penn State University

Mission Statement*: To dramatically increase our fundamental knowledge of the formation and physical interactions of bio-polymer networks in plant cell walls to provide a basis for improved methods for converting biomass into fuels.*



Center theme 1: Understand Cellulose synthesis

Center theme 2: Understand Lignocellulose assembly

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

Theme 1 deals with the mechanism of cellulose synthesis and the nano-scale structure and properties of cellulose. Specific objectives include:

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.

CSC (Cellulose Synthase Complex) function & control: Crystallize the catalytic core of cellulose synthases and develop an X-ray based 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.

Cellulose microfibril structure: Refine models of cellulose microfibril structure by combining experimental spectroscopic data with structural predictions of the computational modeling. Develop sum frequency generation spectroscopy, combined with computational modeling, to refine structural models of cellulose crystalline forms. Experimentally modify cellulose structure through genetic modifications and through the introduction of hemicelluloses and other interacting molecules, to assess the mechanism of microfibril assembly and its impact on cellulose digestibility by defined cellulases. Reconstitute partial or complete cellulose synthase complexes in artificial membranes or nanotubes to assess requirements for glucan and microfibril synthesis and control of microfibril structure.

Theme 2 focuses on how cellulose microfibrils, matrix polysaccharides, structural proteins and lignin assemble to make multifunctional cell walls with unique and diverse properties. Objectives include:

Binding studies: Characterize the dynamics and energetics of specific cellulose-polysaccharide-protein-lignin binding interactions using isothermal titration calorimetry (ITC), surface plasmon resonance techniques and other methods. 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, and use them to assess the impact of matrix polymers on wall assembly and physical characteristics of cell walls.

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 is directed at understanding how the macroscopic properties of cell wall materials emerge from their nano-scale properties and interactions focused on in themes 1 and 2. The following are specific objectives:

Nanoscale characterization and modeling of cell wall structure: Perform computational multiscale modeling of cell walls with application to structural, mechanical, and other physical properties. 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 and study its interaction with wall components. 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), Charles Anderson, Nicole Brown, Jeffrey Catchmark, Vincent Crespi, Gong Chen, Ying Gu, James Kubicki, Teh-hui Kao, Seong Kim, Janna Maranas, B. Tracy Nixon, Virendra Puri, Tom Richard, Ming Tien, Bernhard Tittmann, Linghao Zhong
North Carolina State University	Candace Haigler (Associate Director), Alex Smirnov, Yaroslava Yingling
University of Rhode Island	Alison Roberts
Virginia Tech University	Alan Esker
University of Virginia	Jochen Zimmer

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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 which can be used 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.

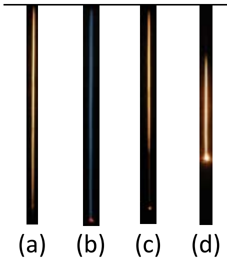
Chemistry/Transport Coupling

- 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)	
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Center for Direct Catalytic Conversion of Biomass to Biofuels (C3Bio)
EFRC Director: Maureen McCann
Lead Institution: Purdue University

Mission Statement*: To integrate fundamental knowledge and enable technologies for catalytic conversion of engineered biomass to advanced biofuels and value-added products.*

Transforming Biomass Utilization for Advanced "Drop-in" Biofuels. Plants fix and chemically reduce carbon dioxide from the atmosphere with high efficiency, using solar energy to construct sugars and aromatic molecules that are stored as lignocellulosic biomass, a renewable resource for domestic energy available from U.S. agriculture and forestry. The major components of biomass are polysaccharides and lignin, the latter accounting for 15 to 25% by weight. Second-generation biofuels are obtained from biomass by using biological catalysis to use the carbon atoms in plant cell wall polysaccharides for the production of ethanol. However, this scenario is both carbon- and energy-inefficient. First, biological conversion routes use only the polysaccharide component of the wall, hydrolyzing polysaccharides to sugars as the carbon source for microbes. Second, the presence of lignin interferes with access of hydrolytic enzymes to polysaccharides, thereby inhibiting their conversion to sugars. Third, only one-third of carbon atoms in the biomass are captured into fuel molecules since living microorganisms required to ferment sugars to biofuels consume some sugars for their own growth and respire carbons as carbon dioxide. Doubling the efficiency would halve the land requirement for growing bioenergy feedstocks. In contrast to biological conversion pathways, the power of chemical catalysis to transform biomass components directly to liquid hydrocarbons and aromatic co-products (third-generation biofuels) is an underexplored area of science that has tremendous potential impact. Our Center aims to make revolutionary advances in the production efficiencies by which biomass carbon is converted into liquid hydrocarbons and other energy-rich molecules by the rational and synergistic design of thermal and chemical conversion processes and the biomass itself.

Research Goals. Our interdisciplinary research team of biologists, chemists and chemical engineers is organized to address four critical roadblocks, our **core goals**:

Core Goal 1: Adding value to lignin by enabling its catalytic conversion. Lignin is an abundant by-product of biorefinery operations, and comprises 40% of the energy content in biomass, but is not utilized to make high-value fuels and co-products. We address knowledge gaps through oxidative and reductive catalytic chemistry to use lignin as a substrate for the production of useful molecules; the ability to analyze lignin and its reaction products; and determining how lignin content, composition and architecture impact the reaction products of thermal or chemical catalyses.

Core Goal 2: Synthesis, assembly and deconstruction of cellulose microfibrils. The structure of the cellulose microfibril, its size, crystallinity and potential aggregation in macrofibrils in plant cell walls, is a second major factor in the recalcitrance of biomass to deconstruction. There is limited understanding of plant microfibril structure, heterogeneity, biochemical mechanism of synthesis, and integration with other matrix polysaccharides and phenylpropanoids. We develop this fundamental knowledge in order to gain control over microfibril synthesis, structure and properties together with the development of catalytic deoxygenation chemistry and selective bond breaking to enable efficient transformations of polysaccharides into useful products.

Core Goal 3: Engineer tailored biomass for highly efficient, direct catalytic conversion to liquid fuels and value-added products. Understanding the processes of wall assembly in the living cell are important to enable 1) formulation of strategies for deconstruction and 2) incorporation of *Trojan horse* catalysts into the cell wall in living plants. A key aspect of catalyst-substrate interactions is the accessibility of catalysts to the chemical bonds with which they are designed to react. We aim to engineer biomass variants to incorporate catalysts, co-catalysts, or functionalized catalytic sites into cell walls as the plant grows, simplifying reaction steps in subsequent processing and alleviating the biphasic barrier between the catalyst in solution and the solid polymeric biomass.

Core Goal 4: Fast-hydropyrolysis to maximize carbon efficiency. Thermal treatments deconstruct biomass into an array of liquid and gaseous products along with some char. However, the bio-oil from fast-pyrolysis has an extremely high oxygen content (35 to 40% by weight), and its energy content is barely half that of petroleum. Fast-hydropyrolysis has the potential to generate intermediate products for catalytic upgrading from highly recalcitrant biomass components. On a systems engineering level, this maximizes carbon efficiency while minimizing the hydrogen inputs necessary for deoxygenation. We aim to develop a detailed understanding of how fast-hydropyrolysis and *in situ* hydrodeoxygenation in the presence of appropriate catalyst(s) can lead to advanced (drop-in) liquid fuels.

Cross-cutting technology resources. Novel mass spectrometric and spectroscopic technologies are being developed for analysis of the products of catalytic reactions with biomass molecules in real time. Using unique National Lab resources, we also are developing an integrated set of powerful imaging techniques and data visualization models to study biomass-catalyst interactions at resolutions ranging from ~200 nm (light microscopy) to Ångström (X-ray).

The transformational knowledge gained will form the basis for novel catalysts and reaction chemistry for conversion of biomass to advanced 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 utilize the current liquid fuel infrastructure and to other high-value hydrocarbon products.

Center for Direct Catalytic Conversion of Biomass to Biofuels (C3Bio)	
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National Renewable Energy Laboratory	Mike Himmel, Michael Crowley, Shi-You Ding, Bryon Donohoe, Mel Tucker
Argonne National Laboratory	Ian McNulty
University of Tennessee	Joe Bozell, Craig Barnes, Alison Buchan
Northeastern University	Lee Makowski

Contact: Maureen C. McCann
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Energy Frontier Research Center for Solid-State Lighting Science (SSLS)

EFRC Director: Michael E. Coltrin

Lead Institution: Sandia National Laboratories

Mission Statement*: To explore energy conversion in tailored photonic structures and materials to enable revolutionary breakthroughs in the efficiency and performance of light emitting diode (LED)-based lighting; to improve energy-efficiency in the way we light our homes and offices, which currently accounts for 20 percent of the Nation's electrical energy use. Solid-state lighting has the potential to cut that energy consumption in half, or even more.*

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.

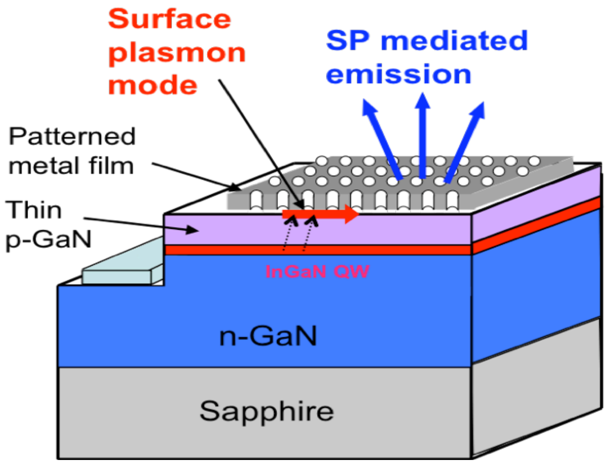

Figure 1. Plasmonic LED structure.

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	
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Northwestern University	L. J. Lauhon
University of California, Merced	D. Kelley
University of California, Santa Barbara	J. Speck
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Heterogeneous Functional Materials for Energy Systems (HeteroFoaM)
EFRC Director: Kenneth Reifsnider
Lead Institution: University of South Carolina

Mission Statement: *To create control science to build a bridge between synthesis and modeling by understanding, designing, and synthesizing heterogeneous functional materials from the atomistic to nano-scale to macro-scale for energy storage and conversion systems such as fuel cells, batteries, supercapacitors, electrolyzers, and solid membranes.*

Material systems consist of hetero-materials arranged in hierarchical architectures (from nano to macro) that significantly facilitate functional performance such as charge and mass transfer along surfaces and across interfaces for chemical and energy transformation processes. Examples include composite mixed-conductors, nano- or micro-structured heterogeneous materials, porous electrodes, nano-structured interfaces and heterostructures, and many other combinations that typically serve as the heart of devices such as fuel cells, electrolyzers, batteries, photovoltaics, catalytic 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 local morphology is a critical element of the material conception and design, and the material is not defined until the synthesis process is selected. **A diagram of our technical approach to these challenges appears in the schematic below.** The left hand side of the chart focuses on how to design the materials (including modeling of properties, performance, synthesis, and processing) and the right hand side of the chart focuses on how the heterogeneous functional systems are made. The backbone of our philosophy is to create a science bridge of relationships (the center of the chart) between how these special heterogeneous materials are made and how they work. Creation of the science bridge needed to do that is the responsibility of our teams of experts, which are focused in three areas, bulk materials design; surface, morphology, and structure design; and evolution of properties and morphology.

Functional materials interact with each other and with the applied electrical, chemical, thermal and mechanical fields applied to them. In that sense, they create material systems.

The special purview of the HeteroFoaM Center is exploitation of multi-scale geometry and arrangements of functional heterogeneous constituents to create material systems with a remarkable range of properties and functionality not bounded by the characteristics of the constituents. Insulating and conducting materials can be mixed together, for example, to create energy storage devices (capacitors) with a capacity increase of six orders of magnitude depending on the material system design, as we have shown. We have also demonstrated that the surfaces, interfaces, and particle sizes in porous electrodes for fuel cells can be designed to reduce energy losses during direct conversion of fuel to electricity by more than twelve orders of magnitude. Other examples are found in over 100 archival papers and 6 patent disclosures filed to date by the HeteroFoaM Team (c.f. **www.HeteroFoaM.com**).

The primary goal of this program is to build a predictive science bridge between how we design Heterogeneous Functional Materials (HeteroFoaMs) with multi-scale models and how we make them work in a prescriptive way. Only the beginning 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 science foundation for understanding those materials to inspire and support the advancement of new creative concepts. That same foundation must also predict the evolution of properties and performance that often controls implementation. And we must create materials design tools for HeteroFoaMs that enable creative, knowledge-based design for prescribed functionality without the expense and time lost by Edisonian methods. The Center structure of this program is essential to make this happen. We cannot build the bridge without the support of a strong integration of the science of materials, surfaces/interfaces, and property and morphology evolution. 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 micro-structure design element of heterogeneous materials. The present approach also recognizes that advances in synthesis and fabrication have brought us to the threshold of controlling local morphology over multiple scales. The HeteroFoaM Center will capture and exploit that new opportunity.

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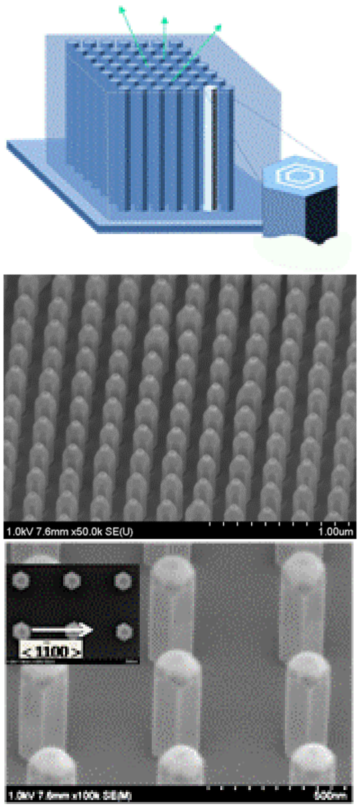
Center for Energy Nanoscience (CEN)
EFRC Director: P. Daniel (Dan) Dapkus
Lead Institution: University of Southern California

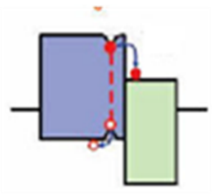
***Mission Statement**: To explore the light absorption and emission in organic and nanostructure materials and their hybrids for solar energy conversion and solid state lighting.*



GaN / InGaN nanorods with nonpolar facets for LEDs. (top) schematic, (middle) GaN nanorod array, (bottom) close-up. of nanorods

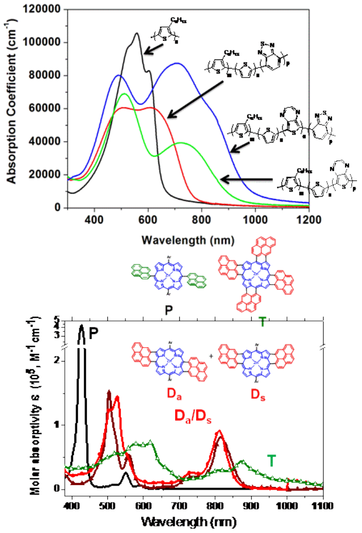
The Center for Energy Nanoscience program to explore emerging materials in solar energy and solid state lighting has as its goals the invention of new solar cell and LED designs based on nanostructured and organic materials. This program is motivated by the following vision: ***to demonstrate new technologies 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 nanostructured semiconductors, organic materials and the resultant novel 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 are to develop the fundamental control of materials and structures at the atomic/molecular scale, understand materials properties and processes at that level to permit the rational design of solar cells and LEDs based on these novel materials, understand interface and structural characteristics that control device performance, and discover the path to the fabrication of devices that demonstrate performance comparable to or exceeding current technology.



Organic Heterostructure Solar Cell Schematic

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 in our Center to exploit the opportunities that we believe will accrue by applying these new materials structures to both solar energy conversion and solid state lighting. We have identified materials technologies [illegible] 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.



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

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.

Center for Energy Nanoscience	
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Center on Nanostructuring for Efficient Energy Conversion (CNEEC)
EFRC Director: Stacey Bent and Fritz Prinz
Lead Institution: Stanford University

Mission Statement: *To understand how nanostructuring can enhance efficiency for energy conversion and to solve fundamental cross-cutting problems in advanced energy conversion and storage systems.*

The overarching goal of the Center is to increase the efficiency of energy conversion by manipulating materials at the nanometer scale. We develop advanced fabrication and characterization methodologies to understand how nanostructuring can optimize light absorption through quantum and optical confinement and improve catalysis through theory-driven design. Each is manipulated to improve performance and efficiency in energy conversion and storage devices.

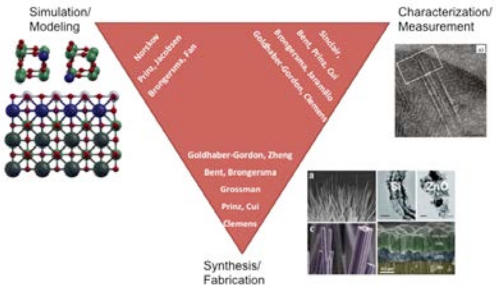

Fig. 1. CNEEC model.

Our research helps provide and expand the scientific foundation of the underlying physical and chemical phenomena shared by a diverse range of energy conversion processes, and exploit them in systems that can lead to break-out high-efficiency, cost-effective energy technologies. Such a multi-disciplinary approach is enabled by the Center structure that provides the intellectual environment and the facilities infrastructure critical to carry out the research projects. A team of CNEEC researchers assembled across disciplines and institutions (see Fig. 1) bring their complementary expertise to bear on these complex but fundamental issues that cut across many energy conversion and storage devices. To pursue its mission, CNEEC has organized its research activities in two interconnected projects:

Project 1. Optical and quantum confinement for light absorption

CNEEC is pioneering the use of optical resonances in high refractive index semiconductor nanostructures for solar applications and in nanometallic (i.e. plasmonic) structures for photoelectrocatalysis. CNEEC is exploring the use of optical resonances in semiconductor and high index oxide nanostructures to ultimately achieve dramatic enhancement in the efficiency of solar absorbers. Properly designed nanostructures and nanostructure-arrays do not require additional light trapping layers as they naturally allow the light to enter and be trapped within the structure. Higher efficiency devices are expected by exploiting these naturally occurring optical (Mie) resonances in semiconductor nanostructures than with the plasmonic approaches pursued thus far. The simple reason for this is that it avoids the undesirable optical (resistive) losses in the nanometallic structures. Despite the tremendous potential, no systematic studies currently exist to optimize ultra thin, nanostructured semiconductor solar absorbers**.** *CNEEC aggressively pursues this new area based on our expertise in the realization of high-efficiency thin film photoelectrochemical (PEC) systems and our leading efforts on the use of the resonances in optical devices.* This project realizes periodic and non-periodic arrangements of nanostructures to enable broadband absorption across the solar spectrum. In collaboration with Project 2, it demonstrates the use of these resonances for the enhancement of oxygen and hydrogen evolution reactions.

In addition to enhancing light absorption by exciting optical resonances in semiconductor nanostructures, CNEEC also exploits quantum size effects to further enhance absorption through bandstructure engineering. This allows one to control where light is absorbed inside the structure using less material. Furthermore, quantum confinement entails a significant modification of the electron and hole wave functions inside a material, leading to the possibility of engineering both the spatial and energetic distribution of charges when designing of next generation solid-state devices. This effort builds upon our recent successes in CNEEC on making and understanding quantum dot structures, including *observing for the first time shape-induced bandgap variations in individual quantum dots*.

Project 2. Atomic scale engineering for catalysis

For all energy conversion technologies that employ catalysts, energy efficiency is directly correlated to catalyst performance. An important goal in CNEEC is to *engineer catalysts with atomic-scale precision* for two key electrochemical energy conversion reactions: (a) water oxidation (oxygen evolution) and (b) hydrogen evolution. Despite decades of research, major technical obstacles still exist in catalyzing these reactions that together effect water-splitting, a potential source of fuel from sunlight, particularly the development of catalysts that are efficient, stable, and that consist of earth-abundant materials. CNEEC takes an approach that triangulates to achieve significant progress: (1) Theory-guided design, where we develop advanced computational models of catalysis on surfaces with predictive power such that one can elucidate specific surface structures, at the level of atoms and electrons, with the desired properties to accelerate the rate of chemical transformations. (2) Inspiration from nature, where we develop methods to study the dynamics of Photosystem II in real time, thereby providing information that can potentially lead to new technologies that rival the capabilities of living things. (3) Atomically-precise methods of catalyst synthesis, where we produce surface structures commensurate with those calculated by theory as well as those that resemble enzymatic catalysts found in nature to be effective for O_2 and H_2 evolution. In this research effort within CNEEC, theory provides guidance as to which surface structures to target, experiments provide feedback to the theory to sharpen and develop the reaction models, and investigation of nature's catalysts help establish design principles for creating new forms of matter with tailored properties for efficient catalysis.

Cross-cutting Themes and Synergy Between Projects

The two projects work together toward the common goal of developing systems that can lead to break-out high-efficiency, cost-effective solar energy-to-fuel technologies. The projects are closely tied together through two mechanisms: (a) physical test systems that integrate light absorption with catalysis, which necessitates the study of interfacial properties and processes that are critical to development of successful absorber-catalyst systems for solar fuel conversion, and (b) the investigation into similar material systems that allow us to leverage the understanding across the projects. CNEEC is working to directly build integrated light absorption structures with catalytic surfaces. The Center pursues studies that cross-cut both projects aimed at understanding interfacial behavior such as defect states, charge transfer properties, and band alignment for the most promising materials discovered in each project. *Our EFRC is aiming to fuse the beneficial effects of quantum and optical confinement in nanostructures to realize higher efficiency photoelectrochemical systems.* In these projects, the length scales that range from the order of 10^2nm (wavelength of light) to 10^1nm (Bohr exciton radius) and 10^0nm (catalytic site dimension) span across both Projects and the physical phenomena they address. The ability to simultaneously build, study, and analyze such integrated nanostructures uniquely offered by CNEEC is crucial for realizing next generation energy systems.

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Northeastern Center for Chemical Energy Storage (NECCES)
EFRC Director: M. Stanley Whittingham
Lead Institution: Stony Brook University

Mission Statement*: To understand how fundamental chemical reactions occur at electrodes and to use this knowledge to design new chemical energy storage 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, what phases are formed, and how the reaction path can be tailored and controlled by appropriate electrode design (doping, particle size, shape, composite structure); identify critical structural and physical properties that are vital to improving battery performance; and use this information to design new battery systems. The role of reaction overpotential will be a unifying theme for all materials. Examples of electrode materials chosen for investigation include doped olivines and conversion chemistries based on the FeF_3-FeOF system. An emphasis is being placed on the development of *in situ* characterization methods that use multiple experimental tools simultaneously or that combine imaging with spectroscopy. Theoretical predictions are being used to determine the most likely reaction routes, and how overpotential and diffusion might control the route and reversibility. To achieve these goals we have established four closely coupled thrusts that enable the necessary synergy and focus on areas of critical relevance to improving energy storage:

Thrust 1: Intercalation chemistry. Experimental studies closely coupled to computational modeling is being used to understand the fundamental ultimate limitations of structure-retention reactions, of both single phase and multi-phase type. Theoretical models have been developed to explain the very high rate of the olivine cathodes, and experiments are underway to determine why partial substitution of the iron has a marked effect on the rate. Cross-over reactions where the initial reaction is intercalation, such as those of lithium with SnCo, FeF_3 and FeOF, and the subsequent conversion are also being studied, thus building a synergistic bridge between thrusts 1 and 2. These studies will, where possible, be performed in-situ so as to study the dynamic system, rather than after relaxation. This will allow the elucidation of the ultimate limits of intercalation reactions, both energy and power, and lead to the key materials criteria for 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 2. 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 with at least three phases being present, sometimes four. All of these phases are in a dynamic state and are 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, and ionic and electronic transport involved at such scales, which allow these systems to operate and to identify kinetically limiting processes. The emphasis is being placed on the Fe-F-O system, and studies to date have shown the criticality of the nanophases formed, both composition and morphology. A good understanding of the phases formed has been obtained. Emphasis is now being placed in two areas. First determining the origin of the high overpotential on cycling, and finding ways to control it. A highly synergistic theory and experimental effort is in place. The second challenge being addressed is how to control the nanostructures formed and in particular their high reactivity.

Thrust 3: **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 the fundamental understanding of electrochemical energy storage systems. The major tool effort is being focused on in-situ studies to specifically address challenges related to understanding the materials in thrusts 1 and 2, and this effort is highly synergistic with the materials and the modeling efforts. These tools are being used to reveal the complex and interdependent processes in electrodes, electrolyte and at their interface. Four major developments are underway: (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, (iii) *in situ* analytical TEM and Electron Energy Loss Spectrometry (EELS) investigations of the electrochemical reactions 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. These studies are utilizing the BES major facilities, including the synchrotrons and nanolabs, available at the Brookhaven, Argonne, Berkeley and Oak Ridge National Laboratories (e.g., for *in* and *ex-situ* PDF, X-ray diffraction, X-ray absorption spectroscopy, TEM and nanofabrication). One example is the development of unique *in situ* transmission electron microscopy/scanning tunneling microscopy that showed, in real-time, the formation of iron nanoparticles, < 5 nm, on reaction of lithium with FeF_2.

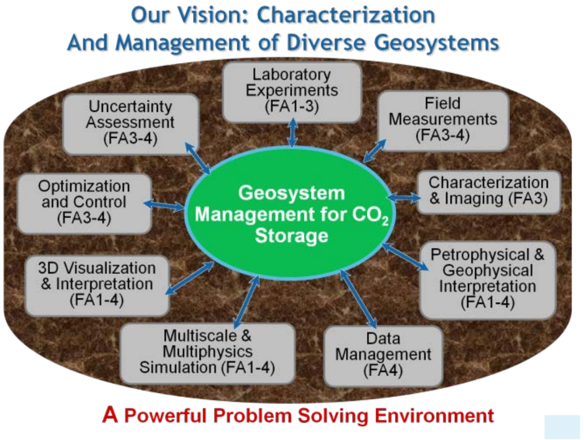
Thrust 4. **Cross-cutting research: Theory and computational modeling to understand and predict kinetic phenomena in electrode materials.** Computational modeling is being used to develop models that predict the rate behavior and reaction paths of electrode materials. A model has been developed that explains the high rate for nano-sized olivine particles, based on a single-phase reaction mechanism. This model identified overpotential as controlling the reaction path, and experiments are underway to test the model. This overpotential model will be broadened beyond structure retention materials such as the olivine and $CuTi_2S_4$ and applied to a range of electrode materials, including the FeF_y conversion materials. The development of this model will also help to guide the discovery of new battery materials with higher power and energy density.

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

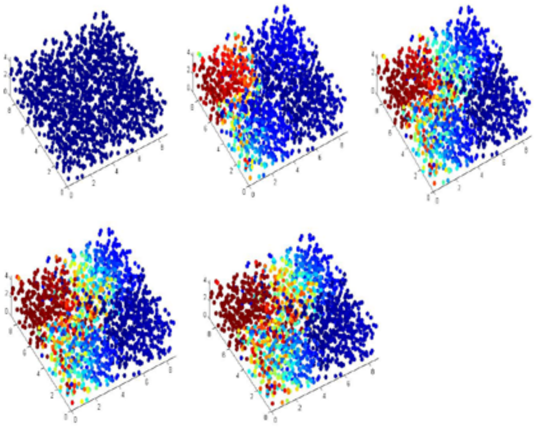
Contact: M. Stanley Whittingham; stanwhit@gmail.com; 631.632.5724; http://necces.chem.sunysb.edu/

Center for Frontiers of Subsurface Energy Security (CFSES)
EFRC Director: Steven Bryant
Lead Institution: The University of Texas Austin

Mission Statement: *To pursue the scientific understanding of multiscale, multiphysics processes and to ensure safe and economically feasible storage of carbon dioxide and other byproducts of energy production without harming the environment.*



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



Concentration field in four coupled pore-scale models

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 key coupled processes 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.

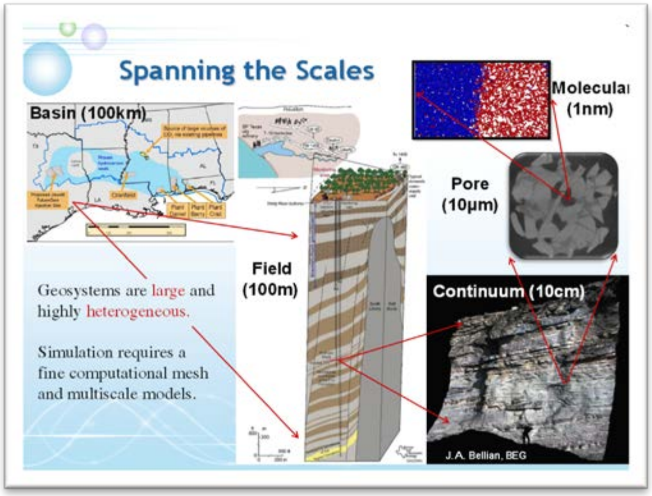
Numerical tools are being developed to:

- 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
- Develop cutting edge techniques for coupling critical phenomena across scales
- Validate the models using laboratory and field observations

This research leverages information from natural analogs, such as the Crystal Geyser, Bravo Dome, and CO_2 injection experiments at the Cranfield, Frio, and in Salah sites.

The research emphasizes the multiphysics at multiscales to understand:

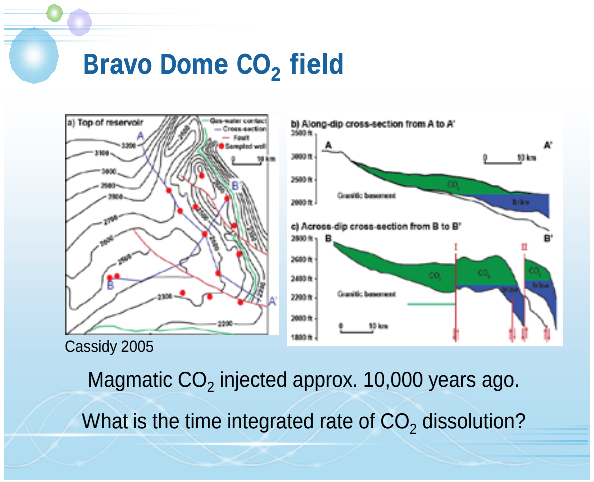
- **the interface between CO_2 and H_2O and other mineral surfaces**
- **the impact of CO_2 and pH change on biomass distribution and flow properties**
- **coupled mechanics, multiphase flow, and reactive transport**



Spanning the Scales

Geosystems are large and highly heterogeneous.

Simulation requires a fine computational mesh and multiscale models.

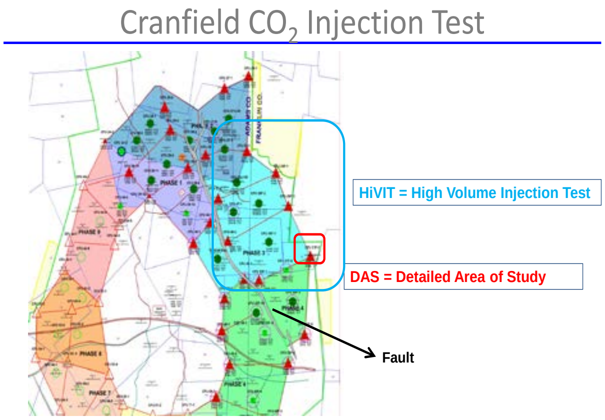


Bravo Dome CO_2 field

Cassidy 2005

Magmatic CO_2 injected approx. 10,000 years ago.

What is the time integrated rate of CO_2 dissolution?



Cranfield CO_2 Injection Test

Center for Frontiers of Subsurface Energy Security (CFSES)	
University of Texas Austin	Steven Bryant (Director), Mary Wheeler (Associate Director), Mojdeh Delshad (Assistant Director), Philip Bennett (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, Gary Pope, Katherine Romanak, Mrinal Sen
Sandia National Laboratories	Marianne Walck (Associate Director), Susan Altman (Assistant Director Manager and Project Leader), Joseph Bishop (Project Leader), Thomas Dewers (Project Leader), Bill Arnold, Randy Cygan, Mario Martinez

Contact: Steven Bryant, Director; steven_bryant@mail.utexas.edu; 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**: To pursue fundamental research on charge transfer processes that underpin the function of highly promising molecular materials for photovoltaic and electrical energy storage applications.*

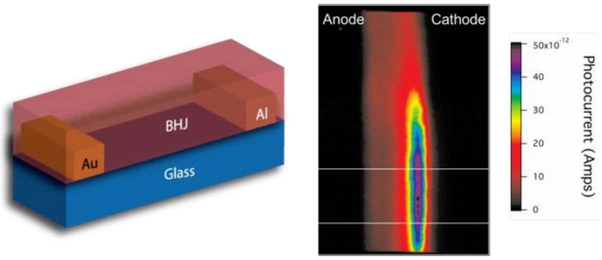
Solar energy conversion and storage are two critical components of a forward-looking strategy to achieve U.S. energy security. This EFRC focuses on a fundamental scientific challenge associated with the development of both organic photovoltaic (OPV) and electrical energy storage (EES) technologies: To understand interfacial charge separation and transfer processes in nanostructured materials at a mechanistic and atomistic level. Progress to date in this area has been limited, in part, by the structural complexity of these materials. They are heterogeneous on the nanoscale, so that conventional probe technique measurements on the meso and bulk scales are incapable of revealing the nano-structural character of these material interfaces, intrinsically limiting the establishment of the structure-property relationships governing these materials for OPV and EES applications. In addition, reliable and feasible theoretical and computational modeling methodologies for describing interfacial charge separation and transfer dynamics in nanostructured materials have not been available. The unique size scale demands that one bridge theoretical approaches between the electronic structure of localized molecular systems and the morphological structure of disordered condensed phase systems. The EFRC:CST was established specifically to overcome these difficulties and hence to markedly advance the fundamental understanding of these charge separation and transfer processes. Three highly coordinated and focused scientific approaches have been implemented:

- 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. Via careful coordination with Approaches 1 & 2, these theoretical/computational efforts are providing insights into the structure of nanomaterial systems, the electronic properties of model interfaces, nonadiabatic charge transfer dynamics, and rate processes at multiple material length and time scales.

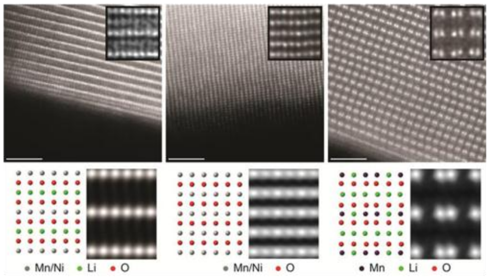
To implement these approaches, we have structured the EFRC:CST into two general thrust areas combining both experiments and theory. Thrust I, **Designing CST Materials and Interfaces,** aims to design, synthesize, and characterize materials and interfaces that we will use to reduce the complexity of 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 complexity from single molecules and single crystals to bulk heterojunctions.

Thrust I: Designing CST Materials and Interfaces:

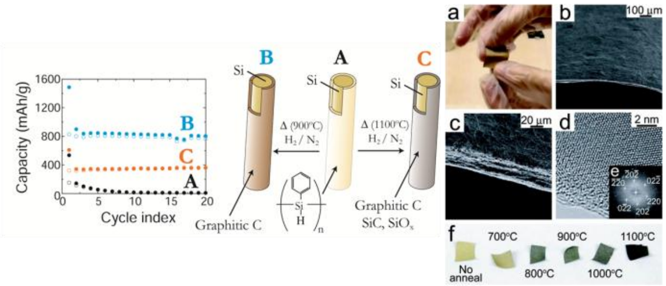
Single-chain, model OPV systems



OPV interfacial prototypes

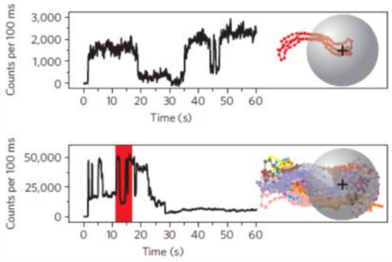


Li-ion battery materials with tunable morphology

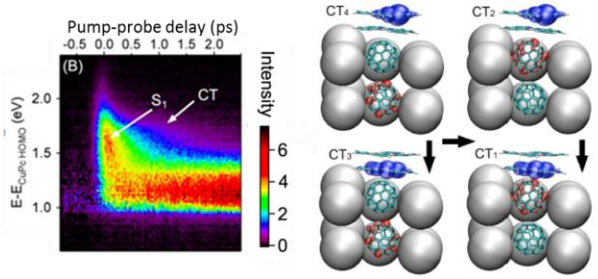


Lightweight, flexible Li-ion battery materials

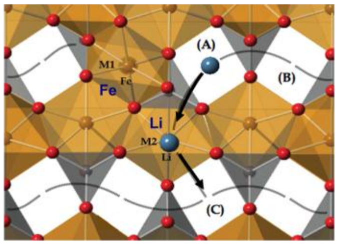
Thrust II: Understanding CST Mechanisms:



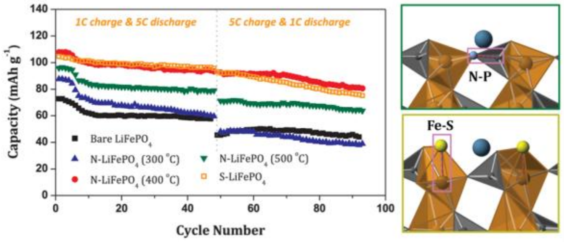
Long-range energy transfer in OPV polymer aggregates



Observation of OPV charge separation dynamics



Concerted Li+ diffusion around anti-site defects



Enhanced charge transfer by surface modification of $LiFePO_4$

Understanding Charge Separation and Transfer at Interfaces in Energy Materials (EFRC:CST)	
University of Texas at Austin	Peter J. Rossky (Director), C. Bielawski, R. Crooks, A. Demkov, A. Dodabalapur, V. Ganesan, J. Goodenough, G. Henkelman, S. Humphrey, B. Holliday, B. Korgel, G. Li, G. Rodin, K. Stevenson, D. Vanden Bout, L. Webb
Sandia National Laboratories	K. Leung, C. Chan
University of California, San Diego	Michael Tauber
University of Minnesota	David Blank

Contact: Prof. Peter J. Rossky, Director EFRC:CST; rossky@mail.utexas.edu; (512) 471-3555
http://www.efrc.nano.utexas.edu

Center for Catalytic Hydrocarbon Functionalization (CCHF)

EFRC Director: T. Brent Gunnoe

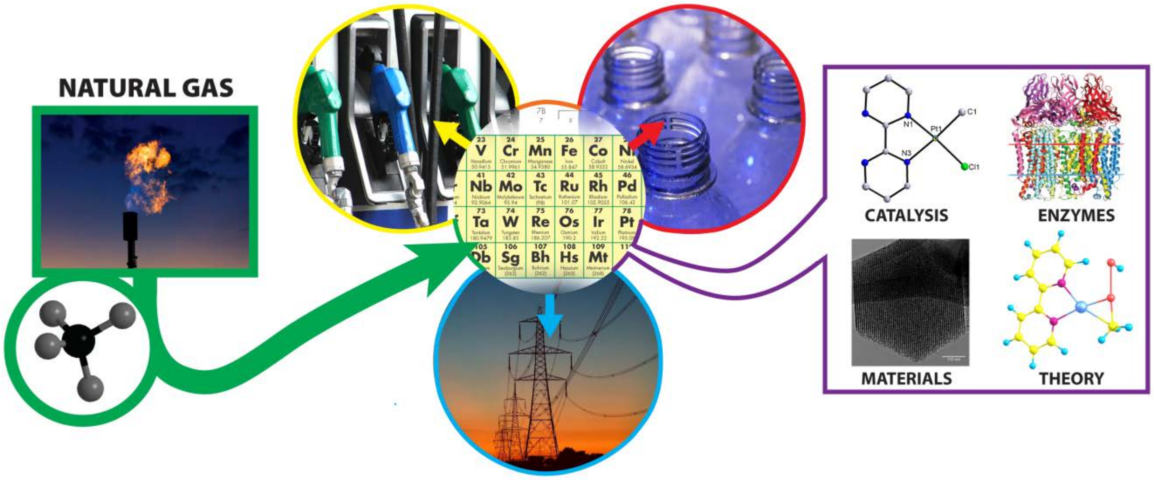
Lead Institution: University of Virginia

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 of hydrocarbons. The current high temperature processes that convert these raw materials into useful products 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, particularly methane from natural gas, 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 reduce our dependence on petroleum through the use of abundant natural gas reserves as our source of liquid fuels and materials, provide cleaner and more energy efficient routes for hydrocarbon processing and lead to the development of high efficiency methane 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.

A major focus of the CCHF is the development of catalysts for the selective and scalable functionalization of methane, with formation of methanol, a versatile liquid fuel, as one desirable target. Another focus is development of anodic catalysts for low temperature direct methane fuel cells, in which methane is oxidized to carbon dioxide and water at low overpotentials and high power. Research in the CCHF is organized into three subgroups: 1) the C–H Activation Subgroup, 2) the Oxygen Activation Subgroup, and 3) the Methane Fuel Cell Subgroup. The unifying element of research in the three subgroups of the CCHF is the development of molecular catalysts for the selective conversion of C–H bonds of hydrocarbons, especially methane, to C–O bonds. All three subgroups employ a combination of computational and experimental methods to rationally design new catalysts.



C–H Activation Subgroup

Research in the C–H Activation Subgroup focuses on development of molecular, single-site transition metal catalysts that activate hydrocarbons (e.g., methane) through reactions that generate a metal-carbon species, which is then functionalized to generate the alcohol or other functional products such as halogenated compounds. Key challenges in catalyst development include: minimizing inhibition and decomposition of catalysts, integration of the C–H activation and metal-carbon functionalization reactions into efficient catalytic cycles, use of dioxygen or air-recyclable oxidant, and minimizing the cost of the catalysts. In addition to designing molecular catalysts for use in solution there is also a focus on supporting these catalysts on nanoparticles.

Oxygen Activation Subgroup

The key distinction between this and the C–H activation subgroup is the underlying mechanism of catalysis. The Oxygen Activation Subgroup focuses on catalysts that activate oxygen to form a reactive metal oxo complex, which can react with hydrocarbons (e.g., methane) to generate functionalized products. Cleavage of C–H bonds by metal oxo complexes often forms a carboradical, and attenuating the lifetime of this radical is critical to selective catalysts. Multiple routes for generation of the reactive metal oxo complex are possible, and work in the CCHF is exploring different pathways, including oxygen atom transfer, electrochemical and photoelectrochemical methods.

Methane Fuel Cell Subgroup

The application of methane fuel cells for electricity generation is currently limited, and the use of methane fuel cells in vehicles is not possible. Key to enabling increased use of methane fuel cells is operation at lower temperatures (<250°C) with high efficiency. This requires the development of stable, efficient electrocatalysts with low overpotentials for the anodic oxidation of methane. Work in the CCHF combines expertise in homogeneous C–H functionalization, electrocatalysis, fuel cells and computational chemistry to design new catalysts for application in direct 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

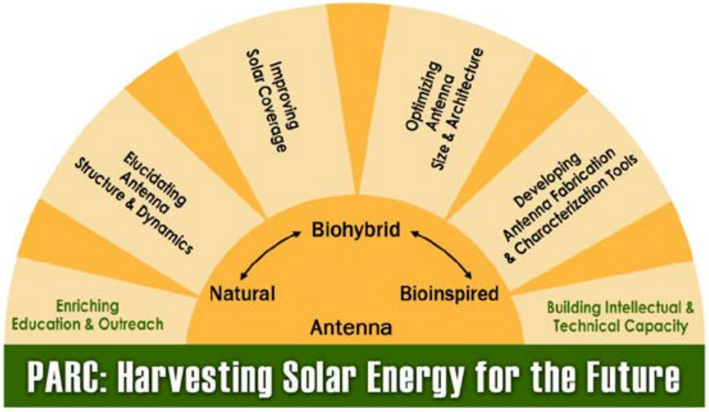
Contact: T. Brent Gunnoe, Director
tbg7h@virginia.edu, (434) 922-2692
http://artsandsciences.virginia.edu/cchf/

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

Mission Statement*: To maximize photosynthetic antenna efficiency in living organisms and to fabricate robust micron-scale biohybrid light-harvesting systems to drive chemical processes or generate photocurrent.*

Scientific Themes. Through basic scientific research, PARC seeks to understand the principles of light-harvesting and energy funneling as applied to three programmatic themes:

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



Unifying Research Activities. The three scientific themes are connected by the idea that enhancements of photosynthetic light harvesting and the design of the biohybid and bioinspired antenna will draw upon the lessons learned from natural systems. The thematic activities are joined by interrelated research threads, including to:

- Elucidate antenna structure and dynamics
- Improve solar coverage
- Optimize antenna size and architecture
- Develop antenna fabrication and characterization tools

Global Impact. All of the PARC activities have the broader goals to:

- Enrich education and outreach
- Build intellectual and technical capacity

Specific Objectives 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, including their efficiency, mechanism of action, regulation, assembly and repair. Emphasis will be placed on developing new and modified antennas using molecular and synthetic biology, such as increasing photosynthetic efficiency by reducing light saturation effects and expanding the spectral ranges of radiation that can be used for energy storage. The specific objectives are to:

- Determine structures of native and modified antenna systems and correlate with function.
- Understand subcellular organization of antenna systems in different photosynthetic organisms.
- Examine physiological consequences of modified/alternate antenna in diverse organisms.

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

Specific Objectives 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) components (e.g., complexes or peptides) are coupled with synthetic components (e.g., substrates or chromophores) . Emphasis will be placed on attachment chemistry, substrate properties, assembly, stability and function. The specific objectives are to:

- Pattern single and multicomponent arrays of bacterial photosynthetic light harvesting complexes on surfaces in various geometries to promote directed energy migration and trapping
- Fabricate biohybrid antenna consisting of peptide analogos of photosynthetic light harvesting complexes coupled with tunable synthetic chromophores to enhance solar coverage.
- Employ genetically and chemically modified biohybrid constructs along with far-and near-field fluorescence microscopy for spectroscopic readout.

The overall aim is to design biohybrid architectures for energy collection and storage.

Specific Objectives for Theme 3: Bioinspired Antennas: Design and Characterization
PARC will draw upon knowledge of native and synthetic antennas to assemble light harvesting arrays for integration into target solar-conversion systems. The aim is fabrication of assemblies that absorb 90% of incident photons over a specified portion of the visible and near-infrared regions and deliver the energy to a target site(s) with a quantum yield of 80% or greater. The specific objectives are to:

- Develop self-assembled macromolecular arrays based on tunable synthetic pigments alone, or incorporated into designer maquette polypeptides.
- Extend the functionality of the arrays to include sites of energy trapping and photochemistry.
- Control mesoscale of constructs using lithographic approaches.

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

The synergy among PARCs principal investigators listed below is extended by 17 Research Affiliates, 5 Scientific Advisory Committee members, 11 research/technical associates, 32 postdoctoral associates, 28 graduate students, 4 undergraduate students, and 5 administrative personnel.

Photosynthetic Antenna Research Center (PARC)	
Washington University in St. Louis	R.E. Blankenship (Director), D. Holten (Associate Director and Theme 3 Lead), H. Pakrasi (Theme 1 Lead), 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
Northwestern University	P. Loach and P. Parkes-Loach
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 Lead)

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

The Basic Energy Sciences Advisory Committee (BESAC) Grand Challenges report, “Directing Matter and Energy: Five Challenges for Science and the Imagination”, identifies the most important scientific questions and science-driven technical challenges facing BES and describes the importance of these challenges to advances in disciplinary science, to technology development, and to energy and other societal needs. Each EFRC addresses one or more of these grand challenges. For more information, see http://science.energy.gov/bes/efrc/research/grand-challenges/.

‘BASIC RESEARCH NEEDS’ INDEX

BES-sponsored workshop reports, conducted from 2003 – 2007, engaged more than 1,500 participants from universities, industry, and DOE laboratories to help identify research directions for a decades-to-century energy strategy. The 46 Energy Frontier Research Centers directly address the use-inspired energy challenges articulated in these reports. For more information, see http://science.energy.gov/bes/efrc/research/basic-research-needs/.

TOPICAL INDEX

EXPERIMENTAL AND THEORETICAL METHODS INDEX

Energy Frontier Research Centers
Technical Summaries

U.S. DEPARTMENT OF ENERGY | Office of Science