

Energy Frontier Research Centers

Impact Report

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INTRODUCTION

Since its inception in 2009, the U. S. Department of Energy's Energy Frontier Research Center (EFRC) program has become an important research modality in the Department's portfolio, enabling high impact research that addresses key scientific challenges for energy technologies. Funded by the Office of Science's Basic Energy Sciences program, the EFRCs are located across the United States and are led by universities, national laboratories, and private research institutions. These multi-investigator, multi-disciplinary centers bring together world-class teams of researchers, often from multiple institutions, 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.

In 2009 five-year awards were made to 46 EFRCs, including 16 that were fully funded by the American Recovery and Reinvestment Act (ARRA). An open recompetition of the program in 2014 resulted in four-year awards to 32 centers, 22 of which are renewals of existing EFRCs and 10 of which are new EFRCs. In 2016, DOE added four new centers to accelerate the scientific breakthroughs needed to support the Department's environmental management and nuclear cleanup mission, bringing the total number of active EFRCs to 36. The impact reports in this document describe some of the many scientific accomplishments and greater impacts of the class of 2009 – 2018 EFRCs and early outcomes from a few of the class of 2014 – 2018 EFRCs.

TABLE OF CONTENTS

Ordered first by Institution and then by Director

Center for Electrochemical Energy Science (CEES) Paul Fenter, Argonne National Laboratory	1
NorthEast Center for Chemical Energy Storage (NECCES) M. Stanley Whittingham, Binghamton University	3
Center for Emergent Superconductivity (CES) Peter Johnson, Brookhaven National Laboratory	5
Light-Material Interactions in Energy Conversion (LMI) Ralph Nuzzo, California Institute of Technology	7
Energy Frontier Research in Extreme Environments (Efree) Russell Hemley, Carnegie Institution of Washington.....	9
Center for Understanding and Control of Acid Gas-induced Evolution of Materials for Energy (UNCAGE-ME) Krista Walton, Georgia Institute of Technology	11
Center for Nanoscale Controls on Geologic CO₂ (NCGC) Donald DePaolo, Lawrence Berkeley National Laboratory	13
Center for Advanced Solar Photophysics (CASP) Victor Klimov, Los Alamos National Laboratory	15
Center for Excitonics (CE) Marc Baldo, Massachusetts Institute of Technology	17
Solid-State Solar-Thermal Energy Conversion Center (S3TEC) Gang Chen, Massachusetts Institute of Technology	19
Center for Next Generation of Materials by Design: Incorporating Metastability (CNGMD) William Tumas, National Renewable Energy Laboratory	21
Center for Bio-Inspired Energy Science (CBES) Samuel Stupp, Northwestern University.....	23
Argonne-Northwestern Solar Energy Research Center (ANSER) Michael Wasielewski, Northwestern University	25
Fluid Interface Reactions, Structures and Transport Center (FIRST) David Wesolowski, Oak Ridge National Laboratory	27
Center for Molecular Electrocatalysis (CME) R. Morris Bullock, Pacific Northwest National Laboratory	29

Center for Lignocellulose Structure and Formation (CLSF)	
Daniel Cosgrove, Pennsylvania State University	31
Center for Direct Catalytic Conversion of Biomass to Biofuels (C3Bio)	
Maureen McCann, Purdue University	33
Center for Mesoscale Transport Properties (m2M)	
Esther Takeuchi, Stony Brook University	35
Center for Gas Separations Relevant to Clean Energy Technologies (CGS)	
Jeffrey Long, University of California, Berkeley	37
Catalysis Center for Energy Innovation (CCEI)	
Dionisios Vlachos, University of Delaware	39
Nanostructures for Electrical Energy Storage (NEES)	
Gary Rubloff, University of Maryland.....	41
Center for Solar Fuels (UNC)	
Thomas Meyer, University of North Carolina	43
Materials Science of Actinides (MSA)	
Peter Burns, University of Notre Dame	45
Center for Frontiers of Subsurface Energy Security (CFSES)	
Larry Lake, University of Texas at Austin	47
Photosynthetic Antenna Research Center (PARC)	
Robert Blankenship, Washington University in St. Louis.....	49

EFRC: CENTER FOR ELECTROCHEMICAL ENERGY SCIENCE (CEES)

UPDATED: AUGUST 2016

AWARDS: \$19.0M (August 2009 – July 2014); \$14.4M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/cees/>; <http://www.anl.gov/cees>

TEAM: Argonne National Laboratory (Lead): Paul Fenter (Director), Khalil Amine, Maria Chan, Larry Curtiss, Jeffrey Elam, Timothy Fister, Christopher Johnson, Michael Thackeray (Deputy Director); **Northwestern University:** Scott Barnett, Michael Bedzyk, Vinayak Dravid, Mark Hersam, Tobin Marks, Christopher Wolverton; **University of Illinois at Urbana-Champaign:** Andrew Gewirth, Ralph Nuzzo, Nancy Sottos, Scott White; **Purdue University:** Jeffrey Greeley.

SCIENTIFIC MISSION AND APPROACH

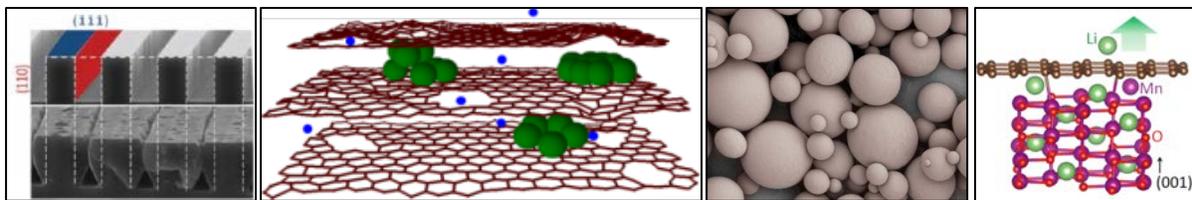
CEES's mission is to create a robust fundamental understanding of the phenomena that control the reactivity of electrified oxide interfaces, films and materials relevant to lithium-ion battery chemistries. Lithium ion batteries are used in personal electronic devices, industrial applications and transportation, yet a substantial fraction of the theoretical properties of the active materials remains unutilized in current lithium ion battery systems due to "side reactions" such as electrolyte decomposition, metastable phases, destabilization of the electrode material, and mechanical degradation. CEES probes the molecular-scale structure at electrified oxide-electrolyte interfaces, leverages advanced materials synthesis to create interfacial systems with well-defined properties (composition, structure, etc.), and develops novel approaches and chemistries to control and direct electrochemical reactivity. The research is divided into two tasks:

The Oxide-Electrolyte Interface: Understand the molecular-scale structure and reactivity of simple oxide-electrolyte interfaces and control that reactivity through interfacial modifications.

Oxide Solid-Phase Electrochemical Reactivity: Understand the thermodynamic and kinetic limitations of electrochemically driven solid-state phase transformations and develop strategies for directing them.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- First to discover that the solid-electrolyte interphase (SEI) contains polymerized electrolyte decomposition products.
- First demonstration of the crystallographically-controlled anisotropy of lithium insertion in silicon, a high capacity electrode that degrades due to extreme volume changes upon lithiation.
- Demonstrated a novel approach to obtain reversible lithiation reactions with multilayer electrode architectures for both alloy anodes (e.g., Si) and metal oxide conversion cathodes (CrO_x).
- Demonstrated encapsulation of silicon nanoparticles by graphene for rapid and reversible cycling having a capacity greater than 1000 mAh/g, far exceeding graphite's capacity of 372 mAh/g. SiNode Systems, a CEES spin-off, is using these concepts to develop automotive batteries.
- Revealed, through joint theoretical and experimental investigations, the fundamental mechanisms of a high-energy density lithium-oxygen prototype battery chemistry using a nanostructured cathode that has a much lower charge overpotential than previous studies.
- Incorporated autonomic processes within electrochemically active lithium ion battery systems to increase safety and lifetime, including local shutdown and conductivity restoration.
- Demonstrated multiple approaches to modify lithium manganese oxide cathodes (e.g., surface doping, graphene functionalization) to control Mn loss during electrochemical cycling.
- Demonstrated new concept of electrochemical stiffness that probes the chemo-mechanical response of electrodes through coordinated stress and strain measurements.



CEES research, from left: Crystallographically-controlled lithiation of silicon; Si/C composite anode architecture used by SiNode; Microspheres that are designed to melt and locally shut down a lithium ion battery when it overheats; Schematic of a graphene functionalized lithium manganese oxide cathode to control secondary reactivity (i.e., Mn loss).

IMPACT

- **SiNode Systems**, a start-up, co-founded in 2012 by Cary Hayner (an EFRC graduate student in Kung's group), is based on intellectual property developed originally within CEES. They have raised \$6.5M in start-up capital through a 2015 DOE Clean Energy Prize, DOE SBIR funding (2013-2014), the US Advanced Battery Consortium (2016), and venture capital. SiNode focuses on commercializing Si/C materials for electric vehicle applications. <http://sinodesystems.com/>
- **ADA Technologies**, founded in 1985, creates and converts innovative technologies to commercial successes. Atomic layer deposition (ALD) solid state electrolytes developed under EFRC funding are currently being evaluated in prototype batteries at ADA. <http://www.adatech.com/>
- **alpha-En Corp**, founded in 1969, is developing a new way to manufacture lithium metal foils for use in lithium batteries. CEES developed solid state electrolyte thin films that Alpha-En is evaluating for use as protective coatings on the lithium metal foils. <http://alpha-encorp.com/>
- **Nanointegris**, co-founded by Hersam in 2007, supplies high-purity, electronically separated nanomaterials. CEES collaborates with Nanointegris on the preparation of carbon nanomaterial additives for composite electrodes. <http://www.nanointegris.com/>
- CEES research accomplishments have been the basis for three SBIR awards.
 - *High Energy Anode Material Development for Li-Ion Batteries* (PIs: Sinode, Cary Hayner, Harold Kung) DOE SBIR Phase I: **\$150K** from Aug 2013 – Jul 2014; DOE SBIR Phase II: **\$1M** from Aug 2014 – Jul 2015
 - *Extreme Long Life High Energy Battery* (PIs: ADA Technologies, Jeffrey Elam) DOD SBIR Phase II: **\$110K** (for EFRC members to conduct R&D in solid state electrolytes) from Aug 2015 – May 2016
- CEES researchers (Pol and Thackeray) were awarded an **R&D 100 Award** for the development of carbon spheres and nanotubes made from plastic waste for battery anodes and lubricating agents.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, CEES had published 137 peer-reviewed publications cited over 5,300 times and filed 21 disclosures, 16 US patent applications, and three foreign patent applications. Six patents have been issued and 1 patent application licensed. The following is a selection of impactful papers:

- Lee, J., Smith, K., Hayner, C. & Kung, H. Silicon nanoparticles-graphene paper composites for Li ion battery anodes. *Chemical Communications* **46**, 2025-2027, doi:[10.1039/b919738a](https://doi.org/10.1039/b919738a) (2010). [**467 citations**]
- Thackeray, M. *et al.* Electrical energy storage for transportation-approaching the limits of, and going beyond, lithium-ion batteries. *Energy Environ. Sci.* **5**, 7854-7863, doi:[10.1039/c2ee21892e](https://doi.org/10.1039/c2ee21892e) (2012). [**517 citations**]
- Esser-Kahn, A., Odom, S., Sottos, N., White, S. & Moore, J. Triggered Release from Polymer Capsules. *Macromolecules* **44**, 5539-5553, doi:[10.1021/ma201014n](https://doi.org/10.1021/ma201014n) (2011). [**257 citations**]
- Lu, J. *et al.* A nanostructured cathode architecture for low charge overpotential in lithium-oxygen batteries. *Nature Communications* **4**, doi:[10.1038/ncomms3383](https://doi.org/10.1038/ncomms3383) (2013). [**165 citations**]
- Goldman, J., Long, B., Gewirth, A. & Nuzzo, R. Strain Anisotropies and Self-Limiting Capacities in Single-Crystalline 3D Silicon Microstructures: Models for High Energy Density Lithium-Ion Battery Anodes. *Advanced Functional Materials* **21**, 2412-2422, doi:[10.1002/adfm.201002487](https://doi.org/10.1002/adfm.201002487) (2011). [**95 citations**]
- Tavassol, H., Jones, E. M. C, Sottos, N. R., Gewirth, A. A, Electrochemical stiffness in lithium-ion batteries, *Nature Materials*, **15**, doi:[10.1038/nmat4708](https://doi.org/10.1038/nmat4708) (2016). [**1 citations**].

EFRC: NORTHEAST CENTER FOR CHEMICAL ENERGY STORAGE (NECCES)

UPDATED: AUGUST 2016

AWARDS: \$17M (August 2009 – July 2014); \$13.3 M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/EFRC/>; <http://necces.binghamton.edu>

TEAM: Binghamton University (Lead): M. Stanley Whittingham (Director), Louis Piper, Guangwen Zhou, Natasha Chernova; **Argonne National Laboratory:** Karena Chapman, Peter Chupas; **Massachusetts Institute of Technology:** Yet-Ming Chiang; **Rutgers, The State University of New Jersey:** Glenn Amatucci, Frederic Cosandey, Philip Batson, Natalie Pereira; **University of Cambridge:** Clare Grey; **University of California, Berkeley:** Gerbrand Ceder; **University of California, San Diego:** Shirley Meng, Shyue Ping Ong; **University of California, Santa Barbara:** Anton Van der Ven; **University of Illinois at Chicago:** Jordi Cabana; **University of Michigan:** Katsuyo Thornton

SCIENTIFIC MISSION AND APPROACH

The mission of NECCES is to develop an understanding of how key electrode reactions occur in cathode materials for Li based batteries, and how they can be controlled to improve electrochemical performance, from the atomistic level to the macroscopic level through the life-time of the operating battery. This mission will allow the determination of the ultimate limits of intercalation reactions for chemical energy storage. The approach and specific research goals of NECCES are to:

1. Attain reversible multi-electron transfer in a cathode material using lithium, using the model compound ϵ -VOPO₄.
2. Close the gap between the theoretical and practical energy density for intercalation compounds, using the model compound LiNi_{0.85}Co_{0.10}Al_{0.05}O₂.
3. Understand performance limiting transport in positive electrode structures from the local through the meso to the macroscale.

To attain these research goals the center is divided into three closely connected and integrated thrusts; the theory effort is integrated into thrusts 1 and 2.

Thrust 1. Intercalation Materials Chemistry: Identify the key materials parameters that are required to optimize intercalation reactions in the bulk active material itself.

Thrust 2. Electrode Transport - Establishing the Local-Meso-Macro Scale Continuum: Establish a comprehensive understanding of the ionic and electronic transport in full electrodes.

Thrust 3. Cross-Cutting Diagnostics: Develop novel *operando* experimental approaches to allow a full understanding of all the reactions occurring in battery materials.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Showed using a combination of theory and experiment that lithium intercalation in the high rate nanosized Olivine LiFePO₄ occurs by a metastable single phase reaction.
- Developed the AMPIX cell that allows meaningful *operando* measurements in electrochemical cells, and used it for elucidating complex structures formed during electrochemical reactions.
- Showed that 2 Li can be reversibly intercalated into a host lattice in a reversible manner, and predicted the most stable phases in the model compound materials Li_xVOPO₄.
- Elucidated the reaction mechanism of conversion cathode materials, such as FeF_y.
- Developed and used NMR tools to reveal type and place of electrodeposited lithium.
- Showed that the charge transfer in layered oxides is a strong function of the lithium content.
- Determined the location and the key roles that Al plays in the layered oxide cathode materials.



NECCES research from left to right: experimental and theoretical profiles of two Li cycling in ϵ -LiVOPO₄, AMPIX cell for in-situ synchrotron studies and techniques employed by NECCES at APS, TEM image and schematic of continuous Fe particle network enabling reversible conversion reaction of FeF₂.

IMPACT

- When NECCES was initiated, the cathode material LiFePO₄ presented a dichotomy. It was an electrical insulator and a one-dimensional Li ion diffuser, yet exhibited an extremely high lithium intercalation and removal. NECCES showed using a combination of theory and experiment, backed up by *operando* cell studies, that nano-sized LiFePO₄ reacts by a single phase mechanism, Li_xFePO₄, and that so long as a high rate of reaction is taking place the lithium ions remain disordered over the lattice sites rather than ordering to form the two phases, LiFePO₄ and FePO₄. This understanding is now being applied to the 2 Li material, Li₂VOPO₄.
- Determined the key parameters controlling and limiting the application of conversion reaction materials, such as FeF_y. This understanding is now being applied to the higher energy density CuF₂.
- NECCES researchers are recognized as world leaders in developing *operando* techniques to understand electrochemical reactions in solid materials. They have been received numerous international awards, including several for junior and mid-career scientists: the ECS Tobias Award (Shirley Meng), the MRS Outstanding Young Investigator Award (Karena Chapman) and the Chemical & Engineering New's Talented Twelve (Karena Chapman).

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, NECCES had published 139 peer-reviewed publications cited over 4,400 times and filed 11 disclosures, 4 US patent applications, and 2 foreign patent applications. 2 patents have been issued and 1 disclosure or patent application licensed. The following is a selection of impactful papers:

- Malik, R., Burch, D., Bazant, M., and Ceder, G. Particle size dependence of the ionic diffusivity. *Nano Letters* **10**, 4123-4127, doi:[10.1021/nl1023595](https://doi.org/10.1021/nl1023595) (2012). [288 citations]
- Xu, B., Fell, C. R., Chi, M., and Meng, Y. S. Identifying surface structural changes in layered Li-excess nickel manganese oxides in high voltage lithium ion batteries: A joint experimental and theoretical study. *Energy & Environmental Sciences* **4**, 2223-2233, doi:[10.1039/C1EE01131F](https://doi.org/10.1039/C1EE01131F) (2011). [298 citations]
- Malik, R., Zhou, F., and Ceder, G. Kinetics of non-equilibrium lithium incorporation in LiFePO₄. *Nature Materials* **10**, 587-590, doi:[10.1038/NMAT3065](https://doi.org/10.1038/NMAT3065) (2011). [210 citations]
- Wang, F., Robert, R., Chernova, N. A., Pereira, N., Omenya, F. O., Badway, F., Hua, X., Ruotolo, M., Zhang, R., Wu, L., Volkov, V., Su, D., Key, B., Whittingham, M. S., Grey, C. P., Amatucci, G. G., Zhu, Y., and Graetz, J. Conversion reaction mechanisms in lithium ion batteries: Study of the binary metal fluoride electrodes. *JACS* **133**, 18828-18836, doi:[10.1021/ja206268a](https://doi.org/10.1021/ja206268a) (2012). [181 citations]
- Hu, Y.-Y., Liu, Z., Nam, K.-W., Borkiewicz, O., Cheng, J., Hua, X., Dunstan, M., Yu, X., Wiaderek, K., Du, L.-S., Chapman, K. W., Chupas, P. J., Yang, X.-Q., and Grey, C. P. Origin of additional capacities seen in metal oxide lithium-ion battery electrodes. *Nature Materials* **12**, 1130-1136, doi:[10.1038/NMAT3784](https://doi.org/10.1038/NMAT3784) (2013). [173 citations]
- Whittingham, M. S. The ultimate limits to intercalation reactions for lithium batteries, *Chemical Reviews* **114**, 11414-11443, doi: [10.1021/cr5003003](https://doi.org/10.1021/cr5003003) (2014). [122 citations]
- Chandrashekar, S., Trease, N. M., Chang, H. J., Du, L.-S., Grey, C. P., and Jerschow, A. 7Li MRI of Li batteries reveals location of microstructural lithium. *Nature Materials* **11**, 311-315, doi:[10.1038/nmat3246](https://doi.org/10.1038/nmat3246) (2012). [105 citations]

EFRC: CENTER FOR EMERGENT SUPERCONDUCTIVITY (CES)

UPDATED: AUGUST 2016

AWARDS: \$22.5M (August 2009 – July 2014); \$14M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/CES/>; <http://www.bnl.gov/energy/ces>

TEAM: Brookhaven National Laboratory (Lead): Peter D. Johnson (Director), John M. Tranquada, J.C. Seamus Davis, Ivan Bozovic, Cedomir Petrovic, Genda Gu, Qiang Li, Mark Dean, Jon Rameau; **Argonne National Laboratory:** Wai Kwok, Michael Norman, Duck Young Chung, Alexei Koshelev, Dean Miller, Ulrich Welp, Mercuri Kanatzidis; **University of Illinois:** Jim Eckstein, Peter Abbamonte, David Ceperley, Philip Phillips, Daniel Shoemaker, Jian-Min Zuo; **Rutgers University:** Gabriel Kotliar; **Florida State University:** Laura Greene; **Los Alamos National Laboratory:** Leonardo Civale

SCIENTIFIC MISSION AND APPROACH

The central mission of the CES is the development of an understanding of high T_c superconductivity (HTS) to enable the prediction and perfection of new HTS materials for use in energy technologies including generation, storage and transmission. Research in the CES is directed towards three key areas:

- 1) **Materials:** Develop new synthesis routes and new theoretical approaches to create new classes of superconducting materials by design.
- 2) **Mechanisms:** Develop a fundamental understanding of the mechanism of high-temperature superconductivity through a range of experimental and theoretical studies.
- 3) **Vortices and Critical Currents:** Develop an understanding of the current carrying limiting processes of existing high-temperature superconductors that will lead to enhanced performance by design.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Molecular Beam Epitaxy was used to invent a new field-effect technology that was applied to HTS to demonstrate that the condensation of pre-formed pairs above T_c drives the transition.
- The first atomic scale visualization of the electronic structure of the “parent” compound of the Fe-based HTS and identification of a nematic phase. These observations were followed up to demonstrate that the pseudogap of copper based HTS is also an electronic nematic.
- Many different Fe-based HTS samples were synthesized and distributed across CES, allowing detailed spectroscopic and transport/thermodynamic studies on the same samples. Systematically mapping out the phase diagrams enabled breakthroughs in HTS vortex-matter research.
- Demonstrated that the cuprate pseudogap phase contains a previously unknown electronic state – a density wave with a d -symmetry form factor. This exotic density wave state may prove to be the key to the existence of the pseudogap phase itself.
- The in-field current carrying capacity of commercial YBCO (HTS) wires was doubled with oxygen-ion irradiation in exposure times that are technologically viable.
- Investigations of vortex pinning at the atomic level in iron based superconductors using ion-irradiation found that the strongest vortex pinning occurs at the metallic-core columnar defects and secondary pinning at clusters of point-like defects.



CES research, from left: superconductor-insulator transition in cuprate thin films driven by field-effect technology; STM measured superconducting gaps in the vortex core region in an FeTeSe superconductor; Momentum resolved electron energy loss spectrometer; Magnetic field dependence of the critical current density J_c demonstrating the critical current enhancement due to ion-irradiation of commercial YBCO coated conductors; Phase diagram of the iron-based superconductor FeTeSe.

IMPACT

- The new *Critical-Current-by-Design* paradigm parallels the Materials Genome Initiative, and provides a rational approach to introducing tailored heterogeneity into commercial HTS superconductors to optimize their current carrying capacity for targeted applications.
- Members of the CES have now given close to 500 invited talks at national and international meetings. CES researchers were responsible for the organizations of the 10th International Conference on Materials and Mechanisms of Superconductivity held in Washington DC, 2012 (The Secretary of Energy was a Plenary Speaker at this event) and the 13th International Workshop on Vortex Matter in Superconductivity held in Chicago 2011.
- Crabtree, Johnson and Greene co-edited a Reports on Progress in Physics *Special Issue on the Fe-based Superconductors* and Johnson co-edited a book on *Iron-based Superconductivity* in the Springer Series in Materials Science. These efforts helped promote CES and HTS internationally.
- Doubling of the critical current by short ion-irradiation times has led to the development of a rapid reel-to-reel irradiation method on commercial HTS wires from **American Superconductor (AMSC)**. This method has launched a viable industrial procedure for enhancing the in-field current carrying capacity of existing post-production wires in a uniform fashion over long lengths. Moreover, the enhanced value of the current density is to the point where they can be used in superconducting rotating machinery. AMSC is one of the leading producers of high T_c superconducting cable in the USA. <http://www.amsc.com/>

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, CES had published 193 peer-reviewed publications cited over 4,300 times and filed 2 disclosures and 2 US patent applications. One disclosure application has been licensed. The following is a selection of impactful papers:

- Chuang, T. -M. *et al.* Nematic Electronic Structure in the "Parent" State of the Iron-Based Superconductor $\text{Ca}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$, *Science* **327**, 181, doi: [10.1126/science.1181083](https://doi.org/10.1126/science.1181083), (2010). [**293 citations**]
- Lawler, M. J., *et al.* Intra-unit-cell electronic nematicity of the high-T_c copper-oxide pseudogap states, *Nature*, **466**, 347-351, doi: [10.1038/nature09169](https://doi.org/10.1038/nature09169) (2010). [**224 citations**]
- Bollinger, A. T. *et al.* Superconductor-insulator transition in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ at the pair quantum resistance, *Nature*, **472**, 458-460, doi: [10.1038/nature09998](https://doi.org/10.1038/nature09998) (2011). [**184 Citations**]
- Leroux, M. *et al.* Rapid doubling of the critical current of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ coated conductors for viable high-speed industrial processing, *Applied Physics Letters* **107**, 192601, doi: [10.1063/1.4935335](https://doi.org/10.1063/1.4935335) (2015). [**5 Citations**]
- Sadovskyy I. A. *et al.* Towards superconducting critical current by design, *Adv. Mater.* **28**, 4593-4600, doi: [10.1002/adma.201600602](https://doi.org/10.1002/adma.201600602) (2016). [**2 Citations**]
- Lv W. *et al.* Orbital ordering and unfrustrated $(\pi, 0)$ magnetism from degenerate double exchange in the iron pnictides, *Phys. Rev. B* **82**, 045125, doi: [10.1103/PhysRevB.82.045125](https://doi.org/10.1103/PhysRevB.82.045125) (2010). [**135 Citations**]
- Huecker M. *et al.* Stripe order in superconducting $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($0.095 \leq x \leq 0.155$), *Phys. Rev. B* **83**, 104506, doi: [10.1103/PhysRevB.83.104506](https://doi.org/10.1103/PhysRevB.83.104506) (2011). [**108 Citations**]

EFRC: LIGHT-MATERIAL INTERACTIONS IN ENERGY CONVERSION (LMI)

UPDATED: AUGUST 2016

AWARDS: \$15.4M (August 2009 – July 2014); \$15.2M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/lmi/>; <http://lmi.caltech.edu/>

TEAM: **California Institute of Technology (lead):** Ralph Nuzzo (Director), Harry Atwater, Andrei Faraon, Nate Lewis, Austin Minnich; **Harvard University:** Jennifer Lewis; **Lawrence Berkeley National Laboratory:** Paul Alivisatos, Eli Yablonovitch, Xiang Zhang; **Stanford University:** Mark Brongersma, Jennifer Dionne, Shanhui Fan; **University of Illinois, Urbana-Champaign:** Paul Braun, Ralph Nuzzo, John Rogers

SCIENTIFIC MISSION AND APPROACH

The LMI EFRC is a national resource for fundamental optical principles and phenomena relevant to solar energy conversion, and for design of new photonic materials and structures used for energy conversion. The overarching goal is to tailor the morphology, complex dielectric structure, and electronic properties of matter so as to sculpt the flow of sunlight and heat, enabling light conversion to electrical energy with unprecedented efficiency. Applying these photonic principles could enable record photovoltaic conversion efficiency and utilization of the entire visible and infrared solar resource. The Center is organized scientifically into four multi-institutional research groups (RGs).

RG1 New Light Management Mechanisms: Exploring new mechanisms and metaphotonic structures for controlling and usefully mediating light-material interactions along with predictive mathematical methods for their inverse design.

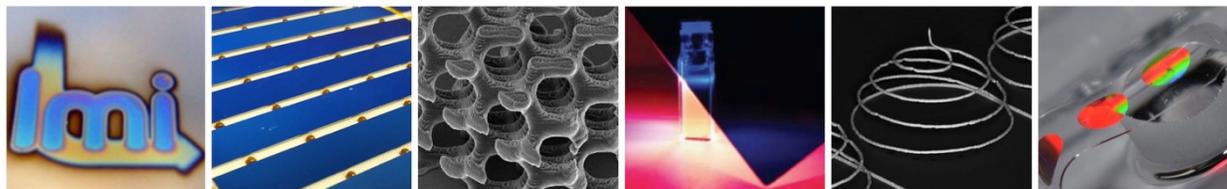
RG2 Solar Spectrum Control and Conversion: Designing photonic principles and fully integrated structures delivering unprecedented capabilities for control and conversion of the solar spectrum to greatly enhance photovoltaic efficiency.

RG3 Thermal Photon Harvesting: Establishing fundamental principles for the utilization and control of thermal photonics, and discovering new structures and materials that enable efficient and useful forms of energy conversion.

RG4 Programmable Assembly of Photonic and Electronic Architectures: Developing powerful new methods for programmable assembly of photonic, electronic, and optoelectronic architectures that yield both materials and device specific elements of enhanced performance.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Discovered new principles of photon emission to maximize photovoltaic conversion efficiencies, providing the foundations of current world record single, dual, and quadruple-junction solar cells.
- Designed photonic crystals with record performance, demonstrating the first optoelectronically active 3D photonic crystal LED and selective thermal emitters with unprecedented stability.
- Advanced quantum dot materials and new principles of photonic design enabling luminescent solar concentrators with record concentration ratios and levels of performance.
- Developed assembly schemes and interface materials for quadruple junction, four terminal solar cells with efficiencies of 44% at concentrations of 1000 suns.
- Developed light-driven material synthesis processes that enable energy conversion materials to develop their own complex architectures in response to illumination conditions.
- Established mathematical methods that enable the design and optimization of photonic structures for light-trapping, spectrum-splitting, and control of near-field thermal emission.



LMI research, from left: refractive index design via porous Si etching; concentrating photovoltaics capturing diffuse and direct irradiance; gyroid photonic crystal fabricated by two-photon lithography; photonic mirror and quantum dot design for luminescent solar concentrators; printed conductive Ag microstructures; conformal metafilm of Si nanoposts.

IMPACT

- **Alta Devices**, co-founded by Atwater and Yablonovitch in 2007, has utilized LMI scientific insights about photon recycling in thin GaAs solar cells to achieve three successive world record open circuit voltages and efficiencies for 1 Sun solar cell conversion efficiency. <http://altadevices.com/>
- **Electroninks Inc.**, co-founded by J. Lewis in 2013, is commercializing reactive silver ink for printed electronics as well as a low-cost roller ball pen filled with conductive silver particle ink, known as Circuit Scribe, for STEM and the DIY/maker communities. The core technology stems from LMI research developing conductive inks. They launched Circuit Scribe using Kickstarter in November 2013 raising \$670,000; and shipped their first products in July 2014. <http://electroninks.com/>
- **MC10**, co-founded by Rogers in 2008, is commercializing stretchable, wearable electronics. LMI work on microcell fabrication and assembly is being explored by MC10. <https://mc10inc.com/>
- **Semprius**, co-founded by Rogers and Nuzzo in 2005, is an innovator in high concentration photovoltaic solar modules. LMI's emerging ideas in stacking, multijunction cells and full spectrum utilization are of direct potential significance to the ultrahigh concentration technology platform that currently serves as the basis for Semprius' commercial modules. <http://semprius.com/>
- **Voxel8**, co-founded by J. Lewis, uses core technology from LMI research on conductive ink development and 3D printed batteries. This VC-backed venture has raised \$14.5M since its inception in Fall 2014, and has grown to more than 25 full-time employees. Voxel8 shipped its first commercial product, a desktop 3D electronics printer in May 2016. <http://www.voxel8.co/>
- LMI research accomplishments have been the basis for more than \$11M in follow-on funding from DOE, including four ARPA-E awards:
 - *Optics for full-Spectrum, Ultrahigh Efficiency Solar Conversion* (PI's: Harry Atwater, Paul Braun, Eli Yablonovitch) at **\$2.4M** from March 2013 to September 2016
 - *Micro-optical Tandem Luminescent Solar Concentrator* (PI's: Ralph Nuzzo, Paul Alivisatos and Harry Atwater) at **\$3.0M** from February 2016 to February 2019
 - *Micro-Scale Ultra-High Efficiency CPV/Diffuse Hybrid Arrays Using Transfer Printing* (PI: John Rogers) at **\$2.9M** from January 2016 to December 2018
 - *Wide-Angle Planar Microtracking Microcell Concentrating Photovoltaics* (PI's: Noel Giebink, John Rogers) at **\$2.9M** from January 2016 to December 2018

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, LMI had published 143 peer-reviewed publications cited over 6,600 times and filed 28 disclosures, 24 US patent applications, and 13 foreign patent applications. One patent has been issued and five patent applications licensed. The top three most highly cited papers are:

- Liu, M. *et al.* A graphene-based broadband optical modulator. *Nature* **474**, 64-67, doi:[10.1038/nature10067](https://doi.org/10.1038/nature10067) (2011). [953 citations]
- Kelzenberg, M. *et al.* Enhanced absorption and carrier collection in Si wire arrays for photovoltaic applications. *Nature Materials* **9**, 239-244, doi:[10.1038/NMAT2635](https://doi.org/10.1038/NMAT2635) (2010). [781 citations]
- Aydin, K. *et al.* Broadband polarization-independent resonant light absorption using ultrathin plasmonic super absorbers. *Nature Communications* **2**, doi:[10.1038/ncomms1528](https://doi.org/10.1038/ncomms1528) (2011). [501 citations]

EFRC: ENERGY FRONTIER RESEARCH IN EXTREME ENVIRONMENTS (EFREE)

UPDATED: AUGUST 2016

AWARDS: \$15.0M (August 2009 – July 2014); \$10.0M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/efree/>; <https://efree.carnegiescience.edu>

TEAM: Carnegie Institution (Lead): Russell Hemley (Director), Timothy Strobel, Stephen Gramsch, Reinhard Boehler, Maria Baldini; **California Institute of Technology:** Brent Fultz; **Colorado School of Mines:** P. Craig Taylor, Lakshmi Krishna; **Cornell University:** Roald Hoffmann, Neil Ashcroft; **George Washington University:** Tianshu Li, Russell Hemley; **Lehigh University:** Kai Landskron; **Pennsylvania State University:** John Badding, Vincent Crespi, Nasim Alem; **University of Tennessee:** Konstantin Lokshin

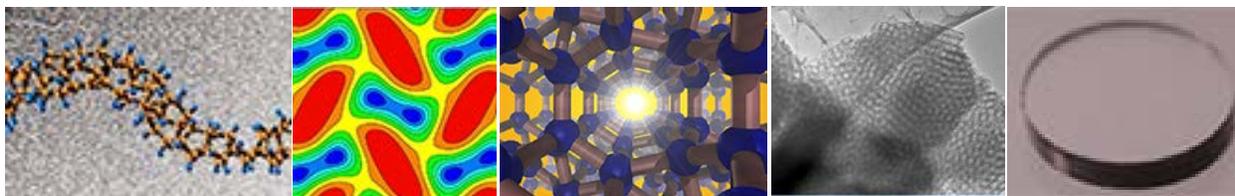
SCIENTIFIC MISSION AND APPROACH

The mission of EFree is to accelerate the discovery and synthesis of new energy materials using extreme conditions. While most materials are created at or near ambient conditions, exploiting extreme environments, notably high pressures and temperatures, has tremendous potential for manipulating matter to synthesize next-generation materials with transformative impacts on energy. Moreover, extreme environments are capable of producing materials with unprecedented mechanical, thermal, and electronic properties. The Center's research projects are organized around three Energy Focus Areas:

- 1) **Advanced Structural Materials:** Use of extreme environments to develop tailored synthetic routes for the discovery, characterization, and preparation of new classes of energy materials such as new nanophase carbons and porous materials
- 2) **Novel Energy Conversion Materials:** Use of extreme environments to create new energy conversion materials and recover them to ambient conditions for enhanced solar energy uptake and other energy conversion applications.
- 3) **Revolutionary Energy Transport Materials:** Use extreme environments to understand the fundamental physics of electron transport in materials, and optimize structure and composition to create new materials with enhanced electrical transport such as high T_c superconductivity.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Carbon nanothreads - a new allotrope of nanocrystalline carbon - was discovered, characterized, and recovered to ambient conditions. The material has chemical bonding properties identical to that of diamond and is considered an ultrastrong, lightweight material with numerous applications.
- A new allotrope of silicon, Si_{24} , having an open-framework structure was developed using a high-pressure precursor method. The material has been recovered at ambient conditions and possesses a quasi-direct band gap making it a potentially highly efficient photovoltaic.
- Porous structures based on dense SiO_2 frameworks were synthesized using a novel high-pressure nanocasting method. The material has accessible mesopores and a wide pore size distribution.
- Metallization and superconductivity was discovered at high pressure in $BaReH_9$, the most hydrogen-rich ionic salt. The result provides key information needed to understand the superconducting properties expected for hydrogen and other hydrogen-rich materials.
- Advanced theoretical calculations predicted the structures, stability, and physical properties of new classes of light element, very high T_c superconductors, including new hydride phases and analog carbon-based superconductors predicted to be stable under ambient pressure.



EFree research, from left: Structure of a one-dimensional carbon nanothread. Electron density map of crystalline dense Li showing an inverse relationship to that of hydrogen. Structure of Si_{24} , showing the open framework structure. TEM image of highly crystalline mesoporous stishovite synthesized using high-pressure nanocasting. Single-crystal diamond window grown by CVD techniques.

IMPACT

- Developments in high-pressure cell designs have enabled neutron diffraction to 100 GPa at the Spallation Neutron Source (SNS). The partnership between EFree and the SNS is yielding advances in both technique development and fundamental science at several neutron scattering beamlines.
- The paper reporting the discovery of carbon nanothreads is in the ISI top 1% for materials science and has been highlighted in many popular scientific publications, newspapers and broadcast news organizations. These materials promise outstanding properties related to their unique high-strength bonding geometry.
- A US patent has been awarded for the development of zeolite-templated carbon (ZTC), a nanostructured material that promotes interactions between molecules physisorbed on its surface at high pressure. ZTC greatly improves physisorption of gases such as CH_4 , C_2H_6 , Kr and CO_2 .
- The paper reporting the synthesis of Si_{24} was the most highly rated paper in *Nature Materials* for papers of similar age, and in the 99th percentile of all papers tracked, as of August 2016. A US patent is pending for the synthesis and several inquiries concerning capital investment have been received.
- Recent advances in CVD diamond growth methods have been put into production at **Washington Diamonds Corporation**, <http://www.wdlabgrowndiamonds.com>. Continued interactions are helping to optimize the growth of material for scientific and technological applications.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, EFree had published 285 peer-reviewed publications cited over 4,500 times and filed two US patent applications and one foreign patent application. One patent has been issued. The following is a selection of impactful papers:

- Fitzgibbons, T. C., Guthrie, M., Xu, E. S., Crespi, V. H., Davidowski, S. K., Cody, G. D., Alem, N. & Badding, J. V. Benzene-derived carbon nanothreads. *Nature Mater.* **14**, 43-47, doi: [10.1038/NMAT4088](https://doi.org/10.1038/NMAT4088) (2015). [43 citations]
- Kim, D. Y., Stefanoski, S., Kurakevych, O. O. & Strobel, T. A. Synthesis of an open-framework allotrope of silicon, *Nature Mat.* **14**, 169-173, doi: [10.1038/NMAT4140](https://doi.org/10.1038/NMAT4140) (2015). [33 citations]
- Naumov, I., Hemley, R. J., Hoffmann R. & Ashcroft, N. W. Chemical bonding in hydrogen and lithium under pressure. *J. Chem. Phys.* **143**, 064702, doi: [10.1063/1.4928076](https://doi.org/10.1063/1.4928076) (2015). [4 citations]
- Boehler, R., Guthrie, M., Molaison, J., dos Santos, A. M., Sinogeikin, S. V., Machida, S., Pradhan, N. & Tulk, C. A. Large-volume diamond cells for neutron diffraction above 90 GPa. *High Press. Res.* **33**, 546-544, doi: [10.1080/08957959.2013.823197](https://doi.org/10.1080/08957959.2013.823197) (2013). [14 citations]
- Niu, H., Chen, X. Q., Wang, S., Li, D., Mao, W. L. & Li, Y. Families of superhard crystalline carbon allotropes constructed via cold compression of graphite and nanotubes. *Phys. Rev. Lett.* **108**, 135501, doi: [10.1103/PhysRevLett.108.135501](https://doi.org/10.1103/PhysRevLett.108.135501) (2012). [75 citations]

EFRC: CENTER FOR UNDERSTANDING AND CONTROL OF ACID GAS-INDUCED EVOLUTION OF MATERIALS FOR ENERGY (UNCAGE-ME)

UPDATED: OCTOBER 2016

AWARDS: \$11.6M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/uncage-me/>; <http://efrc.gatech.edu/>

TEAM: **Georgia Institute of Technology (Lead):** Krista Walton (Director), Michael Filler, Phillip First, Christopher Jones, Ryan Lively, Sankar Nair, Thomas Orlando, David Sholl; **Lehigh University:** Jonas Baltrusaitis, Israel Wachs; **Oak Ridge National Laboratory:** Sheng Dai, Gernot Rother, Tjerk Straatsma, Bobby Sumpter, Zili Wu; **Pennsylvania State University:** Susan Sinnott; **University of Alabama:** David Dixon; **University of Florida:** Sergey Vasenkov; **University of Wisconsin:** JR Schmidt; **Washington University in St. Louis:** Sophia Hayes

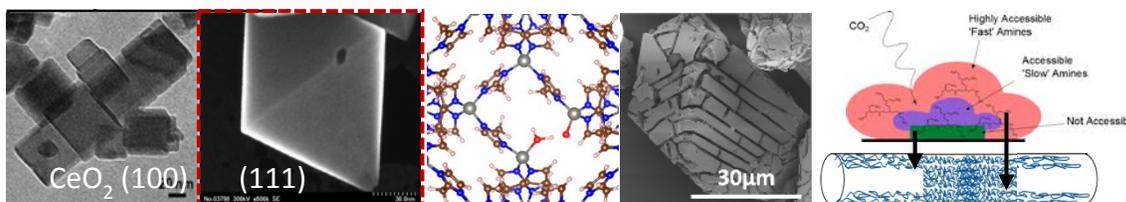
SCIENTIFIC MISSION AND APPROACH

UNCAGE-ME seeks to provide a fundamental understanding of acid gas interactions with solid materials through integrated studies of the interaction of key acid gases (CO₂, NO₂, NO, SO₂, H₂S) with a broad range of materials. The center combines the application of *in situ* molecular spectroscopic studies with complimentary modeling techniques to develop a deep knowledge base with a broad class of materials that will ultimately accelerate materials discovery for large-scale energy applications. The center conducts research in three major thrust areas:

- 1) **Model Metal Oxides:** Develops a molecular level understanding of the surface chemistry of acid gas interactions with model sorbents and catalysts and their structural evolution.
- 2) **Ordered Porous Materials:** Explores the effects of local defects, linkers and metal centers of metal-organic frameworks to tune adsorption interactions and determine structural features that control (in)stability.
- 3) **Disordered Porous Materials:** Seeks to build on knowledge base of model oxide and ordered porous systems to understand heterogeneous systems and to develop a body of knowledge relating support structure/polymer/heteroatom/defects to interaction and stability in the presence of acid gases.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Demonstrated the influence of synthesis methods of state-of-the-art supported metal oxide catalysts for selective catalytic reduction of NO by NH₃: characterizations revealed that unique defect sites were introduced for one synthetic method over the other and resulted in increased catalytic activity.
- Computational characterization of ZIF-8 MOFs found that defects and vacancies provide the starting points for material degradation upon acid gas exposure, which is consistent with observations from model oxide studies.
- Demonstrated the ability to tune kinetic water stability in MOF-74 through proper combination of metal sites while still maintaining high CO₂ adsorption capacities under flue gas conditions.
- Identified distinct differences in the stability of porous organic cages towards SO₂ exposure depending on the chirality of cage linkers and demonstrated stability through use of racemic mixtures.
- Investigations of polymer morphology in aminopolymer-silica composites yielded insights into sorbent efficacy that provide guidelines for the design of sorbent systems with improved kinetics and efficiency for CO₂ capture.



UNCAE-ME research, from left: ceria nanocrystals with well-defined surface facets provide a model system to study acid gas interactions; defects in ZIF-8 are the starting point of acid gas degradation; grain boundaries in porous organic cages accelerate degradation; insights into polymer morphology of aminopolymer-oxide composite sorbents provide guidelines for designing sorbents with improved kinetic performance as well as CO₂ capture efficiency.

IMPACT

- Several EFRC PIs have won national awards including Hayes (2015 ACS Saint Louis Award), Jones (2016 AIChE Andreas Acrivos Award for Professional Progress in Chemical Engineering), Wachs (2015 Lee Hsun Lecture Award of the Chinese Academy of Sciences), and Walton (2015 ACS Women Chemists' Committee Rising Star Award and 2016 AIChE FRI/John G. Kunesh Award for Outstanding Contributions to Separations Technologies)
- Penn State (Sinnott) has developed molecular models and new force field parameters for the COMB3 potential that allows for molecular modeling of titanium carbide-derived carbons. These parameters were distributed to the community via the LAMMPS website. (<http://lammps.sandia.gov/>)
- Georgia Tech (Lively/Sholl) published a perspective article in *J. Phys. Chem. Letters* (reference in the list below) and produced a short YouTube video (with help from Walton) for the American Chemical Society to describe their findings (<https://www.youtube.com/watch?v=1BS2oKeE9aM>). This video was also highlighted in the science blog "The Leap" (<http://www.scilog.com/the-leap/researchers-get-fancy-with-an-iggy-azalea-inspired-journal-submission/>).
- EFRC PI Filler established a new podcast called Nanovation, a forum to address the big questions, challenges, and opportunities of nanotechnology. Sixteen episodes are currently available at <http://www.fillerlab.com/nanovation/>.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of Oct 2016, UNCAE-ME had published 41 peer-reviewed publications cited over 150 times. The following is a selection of impactful papers:

- Holewinski, A.; Sakwa-Novak, M. A.; Jones, C. W. Linking CO₂ Sorption Performance to Polymer Morphology in Aminopolymer/Silica Composites through Neutron Scattering. *Journal of the American Chemical Society* **137**, 11749-11759, doi:[10.1021/jacs.5b06823](https://doi.org/10.1021/jacs.5b06823) (2015). [**12 citations**]
- Jiao, Y. *et al.* Tuning the Kinetic Water Stability and Adsorption Interactions of Mg-MOF-74 by Partial Substitution with Co or Ni. *Industrial & Engineering Chemistry Research* **54**, 12408-12414, doi:[10.1021/acs.iecr.5b03843](https://doi.org/10.1021/acs.iecr.5b03843) (2015). [**11 citations**]
- Sholl, D. S.; Lively, R. P. Defects in Metal-Organic Frameworks - Challenge or Opportunity? *The Journal of Physical Chemistry Letters* **6**, 3437-3444, doi:[10.1021/acs.jpcllett.5b01135](https://doi.org/10.1021/acs.jpcllett.5b01135) (2015). [**22 citations**]
- Tumuluri, U. *et al.* Surface Structure Dependence of SO₂ Interaction with Ceria Nanocrystals with Well-Defined Surface Facets *Journal of Physical Chemistry C* **119**, 28895-28905, doi:[10.1021/acs.jpcc.5b07946](https://doi.org/10.1021/acs.jpcc.5b07946) (2015). [**3 citations**]
- Zhang, C. *et al.* Computational Characterization of Defects in Metal-Organic Frameworks: Spontaneous and Water-induced Point Defects in ZIF-8 *The Journal of Physical Chemistry Letters* **7**, 459-464, doi:[10.1021/acs.jpcllett.5b02683](https://doi.org/10.1021/acs.jpcllett.5b02683) (2016). [**8 citation**]
- He, Y. *et al.* Influence of Synthesis Method on Selective Catalytic Reduction (SCR) of NO by NH₃ with V₂O₅-WO₃/TiO₂ Catalysts *Applied Catalysis B* **193**, 141-150, doi:[10.1016/j.apcatb.2016.04.022](https://doi.org/10.1016/j.apcatb.2016.04.022) (2016) [**2 citations**]
- Zhu, G. *et al.* Engineering Porous Organic Cage Crystals with Increased Acid Gas Resistance *Chemistry- A European Journal* **22**, 10743-10747, doi:[10.1002/chem.201601659](https://doi.org/10.1002/chem.201601659) (2016). [**0 citations**]

EFRC: CENTER FOR NANOSCALE CONTROLS ON GEOLOGIC CO₂ (NCGC)

UPDATED: AUGUST 2016

AWARDS: \$20.0M (August 2009 – July 2014); \$12.8M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/nggc/>; <http://esd1.lbl.gov/research/facilities/nggc/>

TEAM: Lawrence Berkeley National Laboratory (Lead): Don DePaolo (Director), Jonathan Ajo-Franklin, Benjamin Gilbert, Tim Kneafsey, Peter Schuck, Carl Steefel, Tetsu Tokunaga, David Trebotich, Jiamin Wan; **Oak Ridge National Laboratory:** Larry Anovitz, Gernot Rother, Andrew Stack; **Ohio State University:** David Cole; **Princeton University:** Ian Bourg; **Purdue University:** Laura Pyrak-Nolte; **Stanford University:** Sally Benson, Hamdi Tchelepi; **Washington University, St. Louis:** Young-Shin Jun

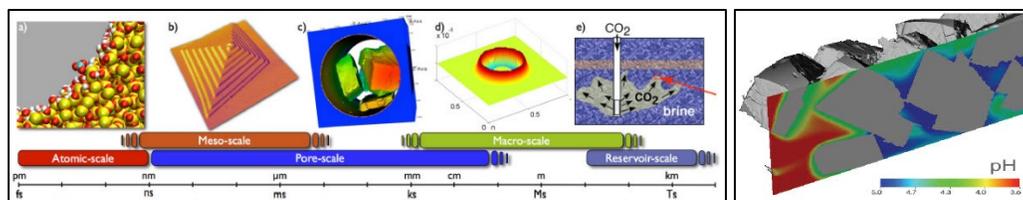
SCIENTIFIC MISSION AND APPROACH

The objectives of NCGC are to provide the fundamental understanding necessary to predict and enhance the performance of underground CO₂ storage systems, and to mitigate problems if they arise during storage operations. Capture and geological sequestration of CO₂ is a potential means of limiting global warming. NCGC uses advanced characterization and modeling tools, combined with specially designed experiments employing purpose-built equipment, to probe the molecular and nanoscale origins of the critical features of fluid-rock systems, with particular reference to CO₂-bearing fluids under carbon storage conditions. The project is organized around three research themes:

- 1) **Fractured Shale:** Discover and characterize the key parameters that determine the effectiveness of fractured shales for sealing CO₂ in the subsurface and preventing release back to the surface.
- 2) **Secondary Trapping:** Quantitatively describe the nanoscale origins, importance and limitations of secondary trapping processes (capillary, dissolution and mineral trapping) for maintaining storage security for long time periods.
- 3) **Mesoscale Modelling Challenge:** Develop the computational tools and insight necessary to model the mesoscale coupling of nanoscale and molecular processes that determine the material properties and dynamics that ultimately are needed to achieve research themes 1 and 2.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Used experiments and modeling to show that shales are robust seals for CO₂, especially when they contain more than 35% clay minerals.
- Determined that organic material and fluid-mineral reactions cause wetting properties to be time-dependent in the subsurface, thus changing the extent of capillary trapping of CO₂.
- Discovered how solution structure and mineral surface templates affect nucleation sites and rates. The studies suggest that preferential nucleation on specific mineral surfaces determines the subsequent porosity and permeability modification in the subsurface.
- Expanded knowledge of supercritical CO₂ (scCO₂)-brine-mineral systems with experiments and theory. Measured the thickness of brine films on mineral surfaces in the presence of scCO₂, with important implications for the efficiency of capillary trapping.
- Developed an approach for determining mineral reactive surface area that combines 3D X-ray CT, 3D FIB-SEM, and 2D Back-Scattered EM, which was then verified with flow-through experiments.
- Developed an experimental-characterization-modeling workflow that creates digital renditions of subsurface pore structure that became the basis for the largest and highest resolution pore-scale reactive transport simulation of CO₂ injection and trapping ever conducted.
- Used SAXS/SANS to demonstrate interplay between CaCO₃ precipitation and nanopore properties.



NCGC research: (left) Carbonate mineral precipitation at various scales. a) Atomic-scale simulation of carbonate adsorption onto a pore wall, b) Single crystal carbonate mineral growth, c) Pore-scale reaction of calcite, d) CO₂ bubble in porous media dissolving host mineral (blue) and precipitating carbonate minerals (red), and e) Illustration of reservoir-scale processes (right) High performance computer simulation results for reactive flow through a CaCO₃-filled capillary tube experiment using computational resources at NERSC, with pore scale structure provided by high resolution X-ray synchrotron microtomography carried out at the Advanced Light Source.

IMPACT

- Edited the 2013 and 2015 *Reviews in Mineralogy and Geochemistry (RiMG)* volumes and conducted associated short courses on pore scale geochemical and mineralogical topics.
- Created new specialized experimental systems that can replicate subsurface conditions and allow for *in situ* and *operando* micro-characterization with X-rays and neutrons.
- Developed, with joint DOE SciDAC funding, new high performance computing tools to model pore-scale fluid flow and chemical reactions.
- Ensured industrial relevance by including advisory board members from BP, Exxon-Mobil, and Shell.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, NCGC had published 123 peer-reviewed publications cited over 2,500 times and filed two invention disclosures. The following is a selection of impactful papers:

- Radha, A. *et al.* Transformation and crystallization energetics of synthetic and biogenic amorphous calcium carbonate. *PNAS* **107**, 16438-16443, doi:[10.1073/pnas.1009959107](https://doi.org/10.1073/pnas.1009959107) (2010). [**136 citations**]
- DePaolo, D. Surface kinetic model for isotopic and trace element fractionation during precipitation of calcite from aqueous solutions. *Geochimica Et Cosmochimica Acta* **75**, 1039-1056, doi: [10.1016/j.gca.2010.11.020](https://doi.org/10.1016/j.gca.2010.11.020) (2011). [**125 citations**]
- Wallace, A. F. *et al.* Microscopic Evidence for Liquid-Liquid Separation in Supersaturated CaCO₃ Solutions. *Science* **341**, 885-889, doi:[10.1126/science.1230915](https://doi.org/10.1126/science.1230915) (2013). [**115 citations**]
- Molins, S., Trebotich, D., Steefel, C. & Shen, C. An investigation of the effect of pore scale flow on average geochemical reaction rates using direct numerical simulation. *Water Resources Research* **48**, doi:[10.1029/2011WR011404](https://doi.org/10.1029/2011WR011404) (2012). [**81 citations**]
- Kim, Y., Wan, J., Kneafsey, T. & Tokunaga, T. Dewetting of Silica Surfaces upon Reactions with Supercritical CO₂ and Brine: Pore-Scale Studies in Micromodels. *Environmental Science & Technology* **46**, 4228-4235, doi:[10.1021/es204096w](https://doi.org/10.1021/es204096w) (2012). [**64 citations**]
- Nielsen, M. H., Aloni, S. & De Yoreo, J. J. In situ TEM imaging of CaCO₃ nucleation reveals coexistence of direct and indirect pathways. *Science* **345**, 1158-1162, doi:[10.1126/science.1254051](https://doi.org/10.1126/science.1254051) (2014). [**86 citations**]
- Cole, D., Chialvo, A., Rother, G., Vlcek, L. & Cummings, P. Supercritical fluid behavior at nanoscale interfaces: Implications for CO₂ sequestration in geologic formations. *Philosophical Magazine* **90**, 2339-2363, doi: [10.1080/14786430903559458](https://doi.org/10.1080/14786430903559458) (2010). [**59 citations**]
- Bourg, I. & Sposito, G. Molecular dynamics simulations of the electrical double layer on smectite surfaces contacting concentrated mixed electrolyte (NaCl-CaCl₂) solutions. *Journal of Colloid and Interface Science* **360**, 701-715, doi:[10.1016/j.jcis.2011.04.063](https://doi.org/10.1016/j.jcis.2011.04.063) (2011). [**57 citations**]
- Shao, H., Ray, J. & Jun, Y. Dissolution and Precipitation of Clay Minerals under Geologic CO₂ Sequestration Conditions: CO₂-Brine-Phlogopite Interactions. *Environmental Science & Technology* **44**, 5999-6005, doi:[10.1021/es1010169](https://doi.org/10.1021/es1010169) (2010). [**51 citations**]

EFRC: CENTER FOR ADVANCED SOLAR PHOTOPHYSICS (CASP)

UPDATED: AUGUST 2016

AWARDS: \$19.0M (August 2009 – July 2014); \$11.2M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/casp/>; <http://casp.lanl.gov>

TEAM: **Los Alamos National Laboratory (Lead):** Victor Klimov (Director), Jeff Pietryga, István Robel, Kirill Velizhanin; **National Renewable Energy Laboratory:** Matt Beard (Associate Director), Justin Johnson, Joey Luther, Art Nozik; **University of California, Irvine:** Matt Law; **University of Minnesota:** Uwe Kortshagen; **George Mason University:** Alexander Efros, Andrew Shabaev; **University of Pennsylvania:** Cherie Kagan; **University of Chicago:** Giulia Galli

SCIENTIFIC MISSION AND APPROACH

CASP’s mission is to investigate and harness the interactions between nanomaterials and light to produce fundamental breakthroughs that will enable the next generation of low-cost, high-efficiency solar energy conversion systems. CASP’s focus is on solution-processible semiconductor nanocrystals, or quantum dots (QDs), that are small enough to exhibit “quantum confinement,” a phenomenon which affects the interactions of these structures with light and each other in profound ways. QD properties can be tailored by varying particle composition, size, shape, internal structure, and inter-particle interactions. CASP is organized into three thrusts:

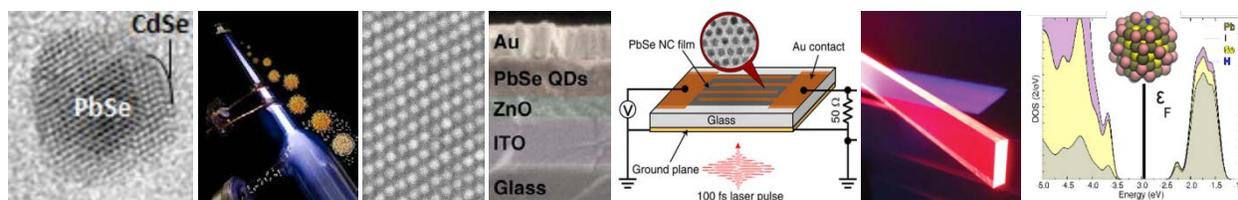
Novel Physical Phenomena: Combines capabilities in optical and scanning-probe spectroscopies emphasizing state-of-the-art femtosecond and single-dot techniques with theory, modeling and simulation including effective-mass, tight-binding, quantum chemistry, and atomistic approaches.

Novel NanoMaterials: Provides advanced capabilities for implementing materials-by-design concepts in the synthesis of engineered nanocrystals and multifunctional nanocomposites using colloidal and plasma-based techniques.

Charge Manipulation and Exploratory Devices: Houses unique capabilities for probing charge transport in mesoscopic QD arrays, as well as for fabrication and characterization of QD-based energy conversion architectures that exploit novel nanoscale physics.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Demonstrated enhanced carrier multiplication (CM) within quantum-confined nanocrystals that allows for the conversion of single high-energy photons into multiple electron-hole pairs and the development of rigorous experimental protocols for quantifying CM efficiencies.
- Demonstrated record-high CM yields in engineered core/shell QDs via suppression of the “cooling” of highly-excited (or “hot”) charge carriers, which competes with multiexciton generation. Foundational stability and charge transport studies of QD films resulted in the demonstration of record-high carrier mobilities via intelligent control of QD surfaces and inter-particle coupling.
- Demonstrated the first stable QD-based solar cells with certified power conversion efficiencies, establishing a new technology class (“quantum-dot solar cells”) on the official PV efficiency chart.
- Made the first solar cell with quantum efficiency greater than 100%, breaking the Shockley-Queisser limit, and confirming that CM enhances the performance of real-life QD-based photovoltaic devices.
- Synthesized a variety of novel engineered nanocrystals, including advanced nanoheterostructures and doped, alloyed, and ligand-free Group IV QDs.
- Developed the underlying principles of QD-based luminescent solar concentrators, and demonstrated efficient devices with dimensions relevant to use as “solar windows.”



CASP research, from left: Heterostructured QDs by colloidal synthesis exhibit tunable optical properties; Plasma synthesis allows Group IV QDs with tunable composition and size; Solution-cast QD films can be highly ordered; PbSe QD solar cells offer extra current via CM; Transient photoconductivity allows for monitoring charge-carrier dynamics in QD films in real time; Luminescent solar concentrators for “solar windows”; Density functional theory connects optical and electronic properties of QDs to the structure of their interior and surfaces.

IMPACT

- CASP has supported and organized multiple international conferences devoted to QD research, including the “7th International Conference on Quantum Dots” (2012), and “20 Years of Quantum Dots at Los Alamos” (2015). CASP has also supported and organized energy- and nanomaterial-focused symposia at national meetings for major scientific societies, including the APS (2015, 2016), MRS (2015, 2011), ACS (2012, 2011), AVS (2011), and AIChE (2011).
- The CASP YIC organizes the biennial “CASP Summer School”. This two-day event is held at a CASP partner site, and brings together an impressive lineup of world leaders in QD and solar energy research for a mixture of topical seminars and direct discussions with local scientists and students.
- **UbiQD, LLC**, is a technology company based in Los Alamos, NM, dedicated to the manufacturing and applications development for luminescent QDs based on non-toxic metals, including copper indium sulfide QDs originally developed for QD-sensitized solar cells within CASP. The company was founded in 2014 by Dr. Hunter McDaniel, former chair of the CASP Young Investigator’s Committee (YIC); a joint CASP-UbiQD publication appeared in *Nature Nanotechnology* in 2015. <http://www.ubiqd.com>

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, CASP had published 146 peer-reviewed publications cited over 10,000 times and filed 6 patent disclosures and 5 US patent applications; 2 patents have been issued. The following is a selection of impactful papers:

- Crisp, R. W., *et al.* Metal halide solid-state surface treatment for high efficiency PbS and PbSe QD solar cells. *Sci. Reports*. **5**, 9945, doi: [10.1038/srep09945](https://doi.org/10.1038/srep09945) (2015). [36 citations]
- Zhang, J., *et al.* PbSe quantum dot solar cells with more than 6% efficiency fabricated in ambient atmosphere. *Nano Lett.* **14**, 6010-6015, doi: [10.1021/nl503085y](https://doi.org/10.1021/nl503085y) (2014) [47 citations]
- Meinardi, F., *et al.* Large-area luminescent solar concentrators based on ‘Stokes-shift-engineered’ nanocrystals in a mass-polymerized PMMA matrix. *Nat. Photon.* **8**, 392-399, doi: [10.1038/nphoton.2014.54](https://doi.org/10.1038/nphoton.2014.54) (2014). [119 citations]
- Wheeler, L. M., *et al.* Hypervalent surface interactions for colloidal stability and doping of silicon nanocrystals. *Nat. Commun.* **4**, 2197, doi: [10.1038/ncomms3197](https://doi.org/10.1038/ncomms3197) (2013). [47 citations]
- McDaniel, H., *et al.* An integrated approach to realizing high-performance liquid-junction quantum dot sensitized solar cells. *Nat. Commun.* **4**, 2887, doi: [10.1038/ncomms3887](https://doi.org/10.1038/ncomms3887) (2013). [79 citations]
- Semonin, O. E., *et al.* Peak external photocurrent quantum efficiency exceeding 100% via MEG in a quantum dot solar cell. *Science* **334**, 1530-1533, doi: [10.1126/science.1209845](https://doi.org/10.1126/science.1209845) (2011). [646 citations]
- Galland, C., *et al.* Two types of luminescence blinking revealed by spectroelectrochemistry of single quantum dots. *Nature* **479**, 203-207, doi: [10.1038/nature10569](https://doi.org/10.1038/nature10569) (2011). [299 citations]
- Liu, Y., *et al.* Dependence of carrier mobility on nanocrystal size and ligand length in PbSe nanocrystal solids. *Nano Lett.* **10**, 1960-1969, doi: [10.1021/nl101284k](https://doi.org/10.1021/nl101284k) (2010). [313 citations]
- Luther, J. M., *et al.* Stability assessment on a 3% bilayer PbS/ZnO quantum dot heterojunction solar cell. *Adv. Mater.* **22**, 3704-3707, doi: [10.1002/adma.201001148](https://doi.org/10.1002/adma.201001148) (2010). [208 citations]

EFRC: CENTER FOR EXCITONICS (CE)

UPDATED: AUGUST 2016

AWARDS: \$19.0M (August 2009 – July 2014); \$14.8M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/ce/>; <http://www.rle.mit.edu/excitonics/>

TEAM: Massachusetts Institute of Technology (Lead): Marc Baldo (Director), Mark Bathe, Mounqi Bawendi, Vladimir Bulovic, Mircea Dinca, Dirk Englund, Pablo Jarillo-Herrero, Jing Kong, Leonid Levitov, Ju Li, Keith Nelson, Gabriella Schlau-Cohen, Will Tisdale, Troy Van Voorhis, Adam Willard; **MIT Lincoln Laboratory:** Eric Dauler; **Harvard University:** Alan Aspuru-Guzik; **Brookhaven National Laboratory:** Charles Black, Eric Stach

SCIENTIFIC MISSION AND APPROACH

CE's mission is to supersede traditional electronics with devices that use excitonics to mediate the flow of energy. Excitons are nanoscale packets of energy that are characteristic of low-cost materials for solar cells and solid state lighting. Conventional materials require long range order and few defects, however excitons can survive in materials like organic molecules, quantum dots and wires, or 2D crystals that have shorter-range order. The room temperature synthesis of these more disordered materials significantly lowers manufacturing costs. CE aims to increase the efficiency of solar cells, and to develop new materials and structures for high brightness solid state lighting. The research is divided into three teams:

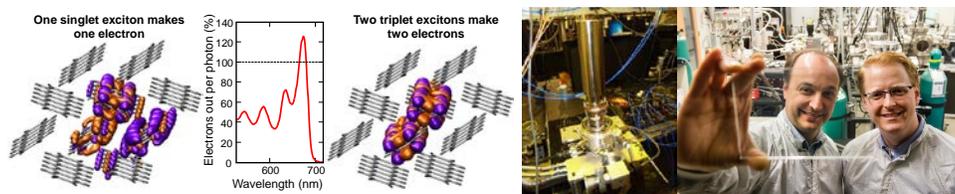
Team 1: Multiexciton Physics and Applications: Seeks to understand and master the dynamics of localized excitons in small molecules and quantum dots for solid state lighting and solar cell applications.

Team 2: Excitonic Antennas and Quantum Transport: Inspired by photosynthesis, study delocalized excited states in molecular assemblies known as excitonic antennas to understand how to protect excitons from long range disorder.

Team 3: Two dimensional Excitonic Crystals: Synthesize and understand the excitonic properties of 2D transition metal dichalcogenides, promising materials for solid state lighting at high brightness.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Used singlet exciton fission to generate multiple carriers in a solar cell at an efficiency of > 1.26 electrons per photon, exceeding the unity limit in conventional electronic materials.
- In conventional nanocrystalline semiconductors, extensive single molecule spectroscopy showed that excitation of secondary electrons must out-compete rapid thermalization losses. However, in molecules, CE demonstrated that these losses are spin disallowed, meaning that exciton fission can be almost perfectly efficient.
- The first demonstration of quantum process tomography on a molecular excitonic system. Experiments unambiguously demonstrated 150 fs coherences and subpicosecond populations transfer between the inner and outer walls of a J-aggregate nanotube, an analogue to a chlorosome.
- The first single-particle spectroscopy of quantum dots in the infrared, an achievement that was made possible by the unique capabilities of CE's superconducting nanowire single photon detectors.
- Realized a hundredfold increase in efficiency of infrared quantum dot-LEDs through improved synthesis and device engineering.
- Developed nano- and atomic-scale methods to visualize exciton transport and annihilation; used the tools to diagnose why droop (low brightness) occurs in quantum dot-based LEDs.



CE research, from left: Unlike electrons, excitons can be split. CE used singlet exciton fission in pentacene to generate at least 1.26 electrons per photon; Superconducting nanowire single photon detector; Vladimir Bulovic and Miles Barr, co-founders of Ubiquitous Energy, show a transparent solar cell that harvests invisible ultraviolet and near-infrared light into electricity.

IMPACT

- **Ubiquitous Energy**, co-founded by Bulovic in 2011, is developing the world's first truly transparent solar technology. The solar cells, first investigated at MIT as part of the CE EFRC, achieve transparency by selectively transmitting visible light, while harvesting invisible ultraviolet and near-infrared light into electricity. Ubiquitous Energy's mission is to eliminate the battery life limitations of mobile devices and power smart glass for buildings. It has won numerous awards, including NSF SBIR/STTR awards and the 2015 Display Week Innovation Award, and has a pilot plant in CA. <http://www.ubiquitous-energy.com/>
- **Photon Spot Inc.**, founded in 2009, specializes in superconducting nanowire single-photon detectors, their applications, and sub-Kelvin cryogenic systems. Photon Spot evaluated CE research on superconducting nanowire single-photon detectors for their business. <http://www.photonspot.com/>
- CE research accomplishments have been the basis for over \$8M in follow-on funding.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, CE had published 202 peer-reviewed publications cited over 5,800 times and filed 31 disclosures, 21 US patent applications, and 12 foreign patent applications. Four patents have been issued and 2 disclosure and patent applications licensed. A selection of highly cited papers are:

- Shirasaki, Y., Supran, G., Bawendi, M. & Bulovic, V. Emergence of colloidal quantum-dot light-emitting technologies. *Nature Photonics* **7**, 13-23, doi:[10.1038/NPHOTON.2012.328](https://doi.org/10.1038/NPHOTON.2012.328) (2013). [404 citations]
- Congreve, D. et al. External Quantum Efficiency Above 100% in a Singlet-Exciton-Fission-Based Organic Photovoltaic Cell. *Science* **340**, 334-337, doi:[10.1126/science.1232994](https://doi.org/10.1126/science.1232994) (2013). [225 citations]
- Gan, X. et al. Chip-integrated ultrafast graphene photodetector with high responsivity. *Nature Photonics* **7**, 883-887, doi:[10.1038/nphoton.2013.253](https://doi.org/10.1038/nphoton.2013.253) (2013). [221 citations]
- Shustova, N. B., McCarthy, B. D. & Dinca, M. Turn-On Fluorescence in Tetraphenylethylene-Based Metal-Organic Frameworks: An Alternative to Aggregation-Induced Emission. *Journal of the American Chemical Society* **133**, 20126-20129, doi:[10.1021/ja209327q](https://doi.org/10.1021/ja209327q) (2011). [180 citations]
- Seo, K. et al. Multicolored Vertical Silicon Nanowires. *Nano Letters* **11**, 1851-1856, doi:[10.1021/nl200201b](https://doi.org/10.1021/nl200201b) (2011). [162 citations]
- Zhao, J., Nair, G., Fisher, B. & Bawendi, M. Challenge to the Charging Model of Semiconductor-Nanocrystal Fluorescence Intermittency from Off-State Quantum Yields and Multiexciton Blinking. *Physical Review Letters* **104**, doi:[10.1103/PhysRevLett.104.157403](https://doi.org/10.1103/PhysRevLett.104.157403) (2010). [144 citations]
- Shustova, N. B., Cozzolino, A. F., Reineke, S., Baldo, M. & Dinca, M. Selective Turn-On Ammonia Sensing Enabled by High-Temperature Fluorescence in Metal-Organic Frameworks with Open Metal Sites. *Journal of the American Chemical Society* **135**, 13326-13329, doi:[10.1021/ja407778a](https://doi.org/10.1021/ja407778a) (2013). [136 citations]
- Wang, K. et al. Trapping and rotating nanoparticles using a plasmonic nano-tweezer with an integrated heat sink. *Nature Communications* **2**, doi:[10.1038/ncomms1480](https://doi.org/10.1038/ncomms1480) (2011). [121 citations]
- Nair, G., Chang, L., Geyer, S. & Bawendi, M. Perspective on the Prospects of a Carrier Multiplication Nanocrystal Solar Cell. *Nano Letters* **11**, 2145-2151, doi:[10.1021/nl200798x](https://doi.org/10.1021/nl200798x) (2011). [119 citations]
- Shim, S., Rebentrost, P., Valteau, S. & Aspuru-Guzik, A. Atomistic Study of the Long-Lived Quantum Coherences in the Fenna-Matthews-Olson Complex. *Biophysical Journal* **102**, 649-660, doi:[10.1016/j.bpj.2011.12.021](https://doi.org/10.1016/j.bpj.2011.12.021) (2012). [112 citations]

EFRC: SOLID-STATE SOLAR THERMAL ENERGY CONVERSION CENTER (S³TEC)

UPDATED: AUGUST 2016

AWARDS: \$17.7M (August 2009 – July 2014); \$12.8M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/s3tec/>; <https://s3tec.mit.edu/>

TEAM: MIT (Lead): Gang Chen (Director), Evelyn N. Wang (Associate Director), Mildred Dresselhaus, Marin Soljacic, Keith Nelson, Yang Shao-Horn, Caroline Ross, Nicolas Hadjiconstantinou, Alexie Kolpak, Liang Fu (Seed Fund); **Boston College:** David Broido; **University of Houston:** Zhifeng Ren; **Northwestern University:** Jeffrey Snyder; **Duke University:** Olivier Delaire; **University of Missouri:** David Singh; **Brookhaven National Laboratory:** Yimei Zhu

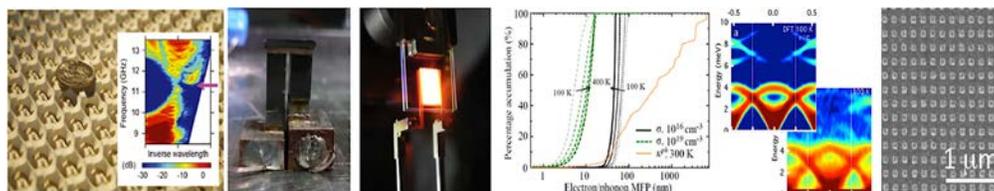
SCIENTIFIC MISSION AND APPROACH

The goals of S³TEC are to advance fundamental science and to develop materials for harnessing heat from the Sun and terrestrial sources and converting this heat into electricity via solid-state thermoelectric, thermogalvanic and thermophotovoltaic technologies. The S³TEC research forms the foundation for understanding thermodynamic and transport processes of photons, phonons, electrons, ions and spins as well as their interactions that increase efficiency of the energy conversion processes. S³TEC advances new materials for the solid-state energy conversion schemes and demonstrates new concepts via experiments. The research is organized around three major thrusts:

- 1) **Electron, phonon, and ion transport:** Develop tools to predict and probe electron, phonon, and ion transport properties that are of vital importance to thermoelectric and thermogalvanic energy conversion.
- 2) **Thermoelectric and thermogalvanic materials:** Design, synthesize, and characterize materials to improve the efficiency of thermoelectric and thermogalvanic energy conversion.
- 3) **High temperature photonics and thermophotovoltaics:** Discover new ways to manipulate photon absorption, emission and reflection to develop high-performance selective absorbers and emitters that are stable at high temperatures for thermophotovoltaic and thermoelectric energy conversion.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Invented spectroscopy techniques to measure phonon mean free path distributions in thermoelectric materials on an optical table.
- Advanced first-principle simulation techniques to enable *ab initio* accurate predictions of all thermoelectric transport properties.
- Observed phonon localization in heat conduction and predicted phonon hydrodynamic modes in 2D materials.
- Discovered semiconducting half-Heuslers with highest power factor, achieved high thermoelectric figure of merit in SnSe-based single crystals (peak ZT ~ 2).
- Made first experimental observation of Weyl points in photonics crystals and of a ring of exceptional points spawned from a single Dirac cone, connecting Dirac physics and non-Hermitian physics.
- Proof-of-principle experiments demonstrated solar thermoelectric generators with efficiencies at 4.6% without optical concentration and 7.4% with optical concentration.
- Proof-of-principle experiments demonstrated solar thermophotovoltaic efficiency at 6.8%.
- Based on fundamental insights into tailoring high-temperature thermal radiation, invented a new type of incandescent light bulb with efficiency that can surpass that of a light emitting diode.



S³TEC research, from left: Weyl points demonstration in photonic crystals; Thermoelectric (TE) generator prototype; novel high-efficiency incandescent light bulb; phonon mean free path measurements (MFP) results for various TE materials; first-principles calculations and neutron and electron beam probing of phonon transport; SEM image of a nanodot structure used in phonon MFP spectroscopy.

IMPACT

- S³TEC students and post-docs are sought-after: 15 of 39 alumni have accepted faculty positions.
- Weyl point in photonic crystals was one of the 2015 Physics World's top ten breakthrough and one of the 2015 American Physical Society's Highlights of the Year; thermally regenerative electrochemical cycles was one of top 10 World Changing Ideas by the Scientific American Magazine in 2014; angular selectivity was one of top 100 science stories of 2014 by Discover Magazine.
- S³TEC organized [OSA Incubator on Fundamental Limits of Optical Energy Conversion](#), featuring speakers from S³TEC and other EFRCs including LMI, CASP and CNGMD. As a result of the event discussions, S³TEC published a [Roadmap on Optical Energy Conversion](#) in the IOP Journal of Optics.
- S³TEC obtained follow-up funding from DOE for the development of high-efficiency solar TE generators (award DE-EE0005806, 2012-2015).
- S³TEC basic research has led to practical applications, as indicated by multiple patent applications and one spin-off company, **Thermoaura Inc.**, which was founded in 2011 and markets high-performance thermoelectric nanomaterials pioneered by the S³TEC researchers: <http://thermoaura.com/>.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, S³TEC had published 313 peer-reviewed publications cited over 11,600 times and filed 46 disclosures, 40 US patent applications, and 27 foreign patent applications. 10 patents have been issued. A selection of highly cited papers are:

- Zebarjadi, M. *et al.* Perspectives on thermoelectrics: from fundamentals to device applications. *Energy & Environmental Science* **5**, 5147, doi: [10.1039/c1ee02497c](https://doi.org/10.1039/c1ee02497c) (2012). [353 citations]
- Kraemer, D. *et al.* High-performance flat-panel solar thermoelectric generators with high thermal concentration. *Nature Materials* **10**, 532–538, doi: [10.1038/nmat3013](https://doi.org/10.1038/nmat3013) (2011). [334 citations]
- Lan, Y. *et al.* Enhancement of thermoelectric figure-of-merit by a bulk nanostructuring approach. *Advanced Functional Materials* **20**, 357–376, doi: [10.1002/adfm.200901512](https://doi.org/10.1002/adfm.200901512) (2010). [330 citations]
- Esfarjani, K., Chen, G. & Stokes, H. Heat transport in silicon from first-principles calculations. *Physical Review B* **84**, doi: [10.1103/PhysRevB.84.085204](https://doi.org/10.1103/PhysRevB.84.085204) (2011). [234 citations]
- Liu, W. *et al.* Recent advances in thermoelectric nanocomposites. *Nano Energy* **1**, 42–56, doi: [10.1016/j.nanoen.2011.10.001](https://doi.org/10.1016/j.nanoen.2011.10.001) (2012). [206 citations]
- Yan, X. *et al.* Experimental studies on anisotropic thermoelectric properties and structures of n-type Bi₂Te_{2.7}Se_{0.3}. *Nano Letters* **10**, 3373–3378, doi: [10.1021/nl101156v](https://doi.org/10.1021/nl101156v) (2010). [201 citations]
- Mehta, R. J. *et al.* A new class of doped nanobulk high-figure-of-merit thermoelectrics by scalable bottom-up assembly. *Nature Materials* **11**, 233–240, doi: [10.1038/nmat3213](https://doi.org/10.1038/nmat3213) (2012). [198 citations]
- Wei, Y. *et al.* The nature of strength enhancement and weakening by pentagon–heptagon defects in graphene. *Nature Materials* **11**, 759–763, doi: [10.1038/nmat3370](https://doi.org/10.1038/nmat3370) (2012). [184 citations]
- Minnich, A. *et al.* Thermal conductivity spectroscopy technique to measure phonon mean free paths. *Physical Review Letters* **107**, 095901, doi: [10.1103/PhysRevLett.107.095901](https://doi.org/10.1103/PhysRevLett.107.095901) (2011). [177 citations]
- Delaire, O. *et al.* Giant anharmonic phonon scattering in PbTe. *Nature Materials* **10**, 614–619, doi: [10.1038/NMAT3035](https://doi.org/10.1038/NMAT3035) (2011). [171 citations]

EFRC: CENTER FOR NEXT GENERATION OF MATERIALS BY DESIGN (CNGMD)

UPDATED: OCTOBER 2016

AWARDS: \$14M (August 2014 – July 2018)

WEBSITES: <http://www.energyfrontier.us/efrc/cngmd>; <http://www.cngmd-efrc.org/>

TEAM: National Renewable Energy Laboratory (Lead): William Tumas (Director), John Perkins (Program Integrator), Dave Ginley (Chief Experimentalist), Stephan Lany, Andriy Zakutayev;
Lawrence Berkeley National Laboratory: Gerbrand Ceder (Chief Theorist), Kristin Persson;
SLAC National Accelerator Laboratory: Michael Toney; **Oregon State University:** Janet Tate;
Harvard University: Daniel Nocera, Roy Gordon; **Colorado School of Mines:** Vladan Stevanovic, Brian Gorman; **Massachusetts Institution of Technology:** Alexie Kolpak, Tonio Buonassisi

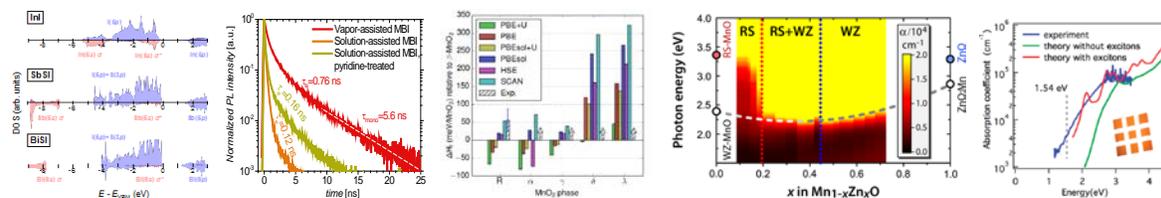
SCIENTIFIC MISSION AND APPROACH

The *vision* of the Center for Next Generation of Materials by Design (CNGMD) is to *dramatically transform the discovery of functional energy materials through multiple-property search, incorporation of metastable materials into predictive design, and the development of specific theory to guide materials synthesis*. The center integrates predictive theory with state-of-the-art high-throughput and directed synthesis and characterization including novel *in-situ* methods to understand and predict structure, properties, and phenomena at the molecular, nano, and meso scales. The focus is on semiconductor materials for renewable energy and energy efficiency applications including solar energy conversion, solid-state lighting, solar fuel production and piezoelectrics. Current research projects are:

- 1) **Pnictide Search** explores new metal nitrides to discover new functional semiconductor materials.
- 2) **Polymorphs and Synthesizability** aims to understand energy landscapes and identify synthetic pathways for specific polymorphs. The focus is on Mn, V and Ti oxides.
- 3) **Chalcogenide Alloys** predicts and guides synthesis of new functional semiconductor alloy materials.
- 4) **Defect Phase Diagrams** derives the defect energies and phase diagram to guide the synthesis of defect-functionalized materials.
- 5) **Perovskite-Inspired Materials Search** designs new materials based on the electronic features of defect tolerance and long carrier lifetimes observed in hybrid organic-inorganic halide perovskites.
- 6) **Piezoelectric Materials Search**, a new project started in 2016, is developing Pb-free piezoelectric materials, including new theoretically predicted metastable materials.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Identified 9 promising materials classes for high defect tolerance based on features of hybrid organic/inorganic perovskites and experimentally showed 5 new materials have desired properties.
- Predicted a number of new nitride materials through theory. Using an activated N source, successfully synthesized metastable binary and ternary nitrides including new binary SnN.
- Predicted and experimentally validated qualitatively new phase diagrams for heterostructural alloys in the MnZnO and SnCaS systems.
- Developed first-principles approaches to predict polymorph stabilities and distributions.
- Predicted and experimentally verified new functionalities in metastable heterostructural alloys compared to isostructural alloys.
- Developed defect phase diagrams to address complex metastable defects and applied to effective electronic doping of Ga₂O₃ with potential applications for wide bandgap electronics.



CNGMD research, from left: Calculated electronic structure of perovskite-inspired PV absorbers; Photo-excited carrier life time measurements for $\text{MA}_3\text{Bi}_2\text{I}_9$; Computed and experimental formation energies of MnO_2 polymorphs; Measured absorption coefficient and calculated band gaps for MnZnO alloys; Calculated and measured optical absorption of metastable Sn_3N_4 .

IMPACT

- **Impact on Materials Genome Initiative (MGI):** CNGMD work on *Perovskite-Inspired Materials* to identify and test promising, non-toxic alternatives to perovskite solar materials called out by White House in *The First Five Years of the Materials Genome Initiative: Accomplishments and Technical Highlights*. CNGMD developed methods being used for applied MGI research including Solar Energy Institute of India and US (<http://www.serius.org>), the NIST-led High-Throughput Experimental Materials Science Virtual Laboratory (<https://mgi.nist.gov>) and several emerging DOE Energy Materials Network consortia (e.g. HydroGEN, Duramat).
- **Outreach, Education and Training:** Organized 2016 Spring MRS symposium “Materials, Interfaces and Devices by Design”. Three CNGMD PI’s were instructors for the associated tutorial attended by 100+ people. Two CNGMD PI’s were lecturers at the International School for Materials for Energy & Sustainability IV (2015) and V (2016). More than 30 invited talks presented by CNGMD scientists. Currently, 13 graduate students and 13 post-docs are working with CNGMD.
- **Publically Released Research Tools and Data:** *Substrate Picker*, a CNGMD developed tool to guide substrate selection for targeted materials synthesis is now available via the Materials Project (<https://materialsproject.org>). Results of CNGMD first-principles material property calculations are available through NREL MatDB (<http://materials.nrel.gov>) and the Materials Project. New *in-situ* experimental tools developed at SLAC now available for general use.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of October 2016, CNGMD had published 20 peer-reviewed publications cited over 130 times and filed 1 US patent application. The following is a selection of impactful papers:

- Sun, W., Dacek, S.T., Ong, S.P., Hautier, G., Jain, A., Richards, W.D., Gamst, A.C., Persson, K.A., Ceder, G., The thermodynamic scale of inorganic crystalline metastability, *Science Advances*, **2**, e1600225, [10.1126/sciadv.1600225](https://doi.org/10.1126/sciadv.1600225) (2016). [0 citations].
- Peng, H., Ndione, P. F., Ginley, D. S., Zakutayev, A. & Lany, S. Design of semiconducting tetrahedral $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ alloys and their application to solar water splitting. *Physical Review X*, **5**, 021016, doi:[10.1103/PhysRevX.5.021016](https://doi.org/10.1103/PhysRevX.5.021016) (2015). [12 citations]
- Brandt, R. E., Stevanovic, V., Ginley, D. S. & Buonassisi, T. Identifying defect-tolerant semiconductors with high minority-carrier lifetimes: beyond hybrid lead halide perovskites. *MRS Communications*, **5**, 265, doi:[10.1557/mrc.2015.26](https://doi.org/10.1557/mrc.2015.26) (2015). [44 citations]
- Brandt, R. E., Kurchin, R.C., Hoye, R.L.Z. *et al.* Investigation of bismuth triiodide (BiI_3) for photovoltaic applications, *J. Phys. Chem. Lett.*, **6**, 4279, doi:[10.1021/acs.jpcclett.5b02022](https://doi.org/10.1021/acs.jpcclett.5b02022) (2015). [11 citations]
- Huynh, M., Shi, C., Billinge, S. J. L. & Nocera, D. G. Nature of Activated Manganese Oxide for Oxygen Evolution. *J. American Chemical Society*, **137**, 14887, doi:[10.1021/jacs.5b06382](https://doi.org/10.1021/jacs.5b06382) (2015). [20 citations]
- Kitchev, D. A., Peng, H., Liu, Y., Sun, J., Perdew, J. P. & Ceder, G. Energetics of MnO_2 polymorphs in density functional theory. *Physical Review B*, **93**, 045132, doi:[10.1103/PhysRevB.93.045132](https://doi.org/10.1103/PhysRevB.93.045132) (2016). [5 citations]
- Ding, H., Dwaraknath, S., Garten, L., Ginley, D. S. & Persson, K. A. Computational approach for epitaxial polymorph stabilization through substrate selection. *ACS Applied Materials and Interfaces*, **8**, 13086, doi:[10.1021/acsami.6b01630](https://doi.org/10.1021/acsami.6b01630) (2016). [2 citations]

EFRC: CENTER FOR BIO-INSPIRED ENERGY SCIENCE (CBES)

UPDATED: AUGUST 2016

AWARDS: \$19.0M (August 2009 – July 2014); \$12.0M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/cbes/>; <http://cbes.northwestern.edu/>

TEAM: Northwestern University (Lead): Samuel Stupp (Director), Chad Mirkin, Monica Olvera de la Cruz, Mark Ratner, George Schatz, Igal Szleifer, Emily Weiss; **Columbia University:** Kyle Bishop; **Harvard University:** George Whitesides; **New York University:** Paul Chaikin; **University of Michigan:** Sharon Glotzer; **University of Pittsburgh:** Anna Balazs

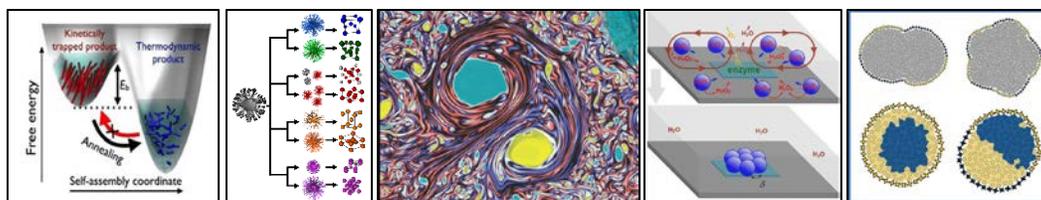
SCIENTIFIC MISSION AND APPROACH

The goal of the Center for Bio-inspired Energy Science (CBES) is to develop artificial materials and systems that take inspiration from biology to optimize the way we use energy and interconvert between different energy forms, for example converting chemical energy into mechanical energy the way muscles do in living organisms. The center consists of three thrusts:

- 1) **Materials with Bio-Inspired Functions** focuses on materials with biomimetic functions related to inter-conversion between chemical and mechanical energy forms (as muscles do), particles inspired by biological organelles that utilize feedback mechanisms to mediate chemical reactions, and the development of adaptive materials.
- 2) **Colloidal Machines** investigates active matter in the form of colloidal machines, which are systems of nanometer to micrometer scale colloids that behave collectively far from equilibrium.
- 3) **Bio-Inspired Transport of Energy and Charge** explores artificial matter that could exhibit bio-inspired mechanisms of electron and ion transport, such as those of transmembrane ion pumps, electronic ratchets, and photosynthetic systems.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Inorganic nanoparticles covered with complementary DNA strands can assemble into 20 different lattice symmetries and a wide variety of lattice constants that had not previously been possible with other nanoscale assembly schemes. Unlike other methods, the crystalline structures are fully “programmable” depending on the sequences of the DNA strands mediating nanoparticle assembly.
- Energy landscapes of peptide amphiphile and chromophore amphiphile assemblies can be controlled to determine their function. Molecular dynamics simulations capture differences in assembly between pathways, such as density of β -sheet hydrogen bonds.
- Mechanically bistable molecules were developed that display dissipative transitions between metastable states. Transitions between these states provide switching functions that can be combined with external forces or light to make molecular machines.
- Muscle tissue is a remarkable hierarchically organized material, the foundation of which rests on the ability of motor proteins to convert chemical energy into mechanical motion. A novel family of molecular machine prototypes known as daisy chains were developed that express large-amplitude length changes in response to thermal or electrochemical stimuli. These mechanical motions resemble the extension and contraction of a sarcomere, the basic functional unit of muscle tissue.
- Nanostructures were developed to demonstrate the energy conversion of plasmonic excitations (short-lived and highly-dissipative but collective and strong) into a photocurrent or to drive chemical reactions in solution. Theoretical work suggests that such a conversion is not possible without concentrating the energy within a small region of space.



CBES research, from left: preparative pathway of self-assembled supramolecular systems can determine their final position in their energy landscape; transmutable nanoparticles are building blocks with different possible binding characteristics that can be selectively activated and deactivated; self-propelled vortex doublets within mixtures of actively rotating fluids; reactions catalyzed by surface-bound enzymes generate fluid flow, causing reagent-laden microcapsules to aggregate; and model of “colloidal cells” from active particles.

IMPACT

- Public CBES Research Symposium held at Northwestern University, July 31, 2015, featured guest speakers Joanna Aizenberg from Harvard University and Juan de Pablo from the University of Chicago and selected CBES investigators. 66 students and post-docs attended.
- Gordon Research Conference on “Complex Active & Adaptive Material Systems: Designing Biomimetic, Dissipative Material Systems” will be held Jan. 29-Feb. 3, 2017 in Ventura, California (Anna C. Balazs, Chair; will include research presentations by five different CBES faculty).
- Endowment funds totaling \$5 million were provided to Northwestern to build a dedicated facility for CBES because of the donors’ interest in the concept of bio-inspired energy science. CBES administration and part of its research activities will be localized in this new space at Northwestern.
- Out of 86 alumni in permanent jobs, 53 now have academic positions, 31 work in industry, and 2 have government positions.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, CBES had published 350 peer-reviewed publications cited over 13,300 times and filed 22 disclosures, 13 US patent applications, and 8 foreign patent applications. One patent has been issued and five disclosures or patent applications have been licensed. The following is a selection of impactful papers:

- Tagliazucchi, M., Azzaroni, O., Szleifer, I. Responsive Polymers End-Tethered in Solid-State Nanochannels: When Nanoconfinement Really Matters. *Journal of the American Chemical Society* **132**, 12404-12411 doi:[10.1021/ja104152g](https://doi.org/10.1021/ja104152g) (2010). [**62 citations**]
- Morris-Cohen, A. J., Frederick, M. T., Lilly, G. D., McArthur, E. A., Weiss, E. A. Organic Surfactant-Controlled Composition of the Surfaces of CDSE Quantum Dots. *Journal of Physical Chemistry Letters* **1**, 1078-1081 doi:[10.1021/jz100224q](https://doi.org/10.1021/jz100224q) (2010). [**67 citations**]
- Baytekin, H. T.; Patashinski, A.; Branicki, M.; Baytekin, B., Soh, S., Grzybowski, B. A. Mosaic Of Surface Charge In Contact Electrification. *Science* **333**, 308, doi:[10.1126/science.1201512](https://doi.org/10.1126/science.1201512) (2011). [**167 citations**]
- Coskun, A., Banaszak, M., Astumian, R. D., Stoddart, J. F., Grzybowski, B. A. Great Expectations: Can Artificial Molecular Machines Deliver on Their Promise? *Chemical Society Reviews* **41**, 19-30, doi:[10.1039/c1cs15262a](https://doi.org/10.1039/c1cs15262a) (2012). [**327 citations**]
- Demirors, A. F., Pillai, P. P., Kowalczyk, B., Grzybowski, B. A. Colloidal Assembly Directed by Virtual Magnetic Moulds. *Nature* **503**, 99-103, doi: [10.1038/nature12591](https://doi.org/10.1038/nature12591) (2013). [**56 citations**]
- Tantakitti, F., Boekhoven, J., Wang, X., Kazantsev, R., Yu, T., Li, J., Zhuang, E., Zandi, R., Ortony, J. H., Newcomb, C. J., Yu, T., Palmer, L. C., Shekhawat, G. S., Olvera de la Cruz, M., Schatz, G. C., Stupp, S. I. Energy landscapes of peptide amphiphiles determine their function. *Nature Materials* **15**, 469–476, doi:[10.1038/nmat4538](https://doi.org/10.1038/nmat4538) (2016). [**11 citations**]

EFRC: ARGONNE-NORTHWESTERN SOLAR ENERGY RESEARCH CENTER (ANSER)

UPDATED: AUGUST 2016

AWARDS: \$19.0M (August 2009 – July 2014); \$15.2M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/anser/>; <http://www.ansercenter.org>

TEAM: Northwestern University (Lead): Michael Wasielewski (Director), Michael Bedzyk, Robert Chang, Mark Hersam, Joseph Hupp, Mercuri Kanatzidis, Tobin Marks, Mark Ratner, George Schatz, Samuel Stupp, Emily Weiss; **Argonne National Laboratory:** Lin Chen, Alex Martinson, Michael Pellin, David Tiede; **Yale University:** Gary Brudvig, Robert Crabtree, Victor Batista, James Mayer; **University of Chicago:** Luping Yu; **University of Illinois, Urbana-Champaign:** Sharon Hammes-Schiffer

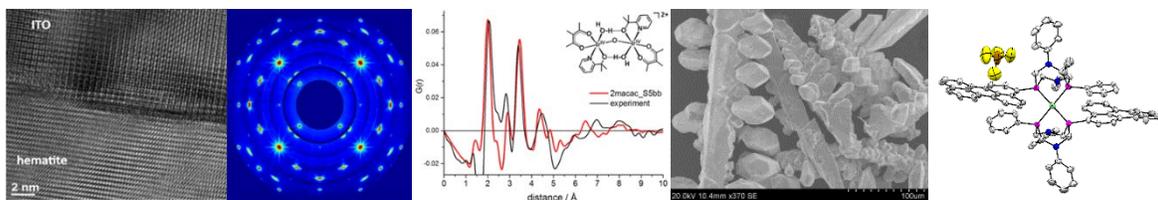
SCIENTIFIC MISSION AND APPROACH

The ANSER Center focuses on understanding how molecules, materials, and systems can use sunlight to generate charges that drive catalysts for solar fuels formation and directly power photovoltaic cells. The center addresses a common set of fundamental questions that must be answered in both contexts to successfully utilize sunlight as a renewable energy source for fuels and electricity. By attacking the common questions intrinsic to solar fuels and electricity in the same research center, ANSER provides opportunities for crosscutting solutions not possible by addressing only fuels or electricity alone. The long-term vision of the ANSER Center is to develop the fundamental understanding, materials and methods necessary to create dramatically more efficient technologies for solar fuels and electricity production. This vision is realized by understanding and characterizing the basic phenomena of solar energy conversion dynamics, by designing and synthesizing new nanoscale and mesoscale 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. The center consists of two thrusts:

- 1) **Solar fuels:** A hierarchical approach to understanding catalyst and photocatalyst function is used to realize efficient solar fuel production (from water-splitting and CO₂ reduction) at acceptable rates and driving forces.
- 2) **Solar electricity:** Fabrication of photovoltaic cells from relatively simple, non-toxic, Earth-abundant, and low-cost materials affording large-scale solar electricity production in the future.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- First to demonstrate an all-solid-state dye-sensitized solar cell, based on perovskites, with a power conversion efficiency greater than 10%, launching a flurry of research on perovskite solar cells.
- Found that replacing the uniform self-assembled monolayer on the anode in an organic photovoltaic cell with a “supersaturated” heterogeneous monolayer increases the power conversion efficiency 54% due to superior charge selectivity and collection.
- Synthesized a rare form of iron oxide and showed it is one of only a few feasible water oxidation photoanodes. ANSER also discovered that a common form of iron oxide, functionalized with iridium water-oxidation catalysts, can use the sun to split water into hydrogen and oxygen in acidic solutions.
- Discovered that nickel-sulfide catalysts deposited within metal organic framework (MOF) films exhibit enhanced hydrogen production compared to MOF-free versions due to the local MOF environment.
- Used theory to discover an amphiphilic organic molecule, used in solar fuel cells, with the optimal structure to facilitate the electron-transfer processes that occur during hydrogen production.
- Demonstrated that ternary organic components, which expand the spectral range of light absorption, improved the power conversion efficiency of bulk heterojunction solar cells by 20%.



ANSER research, from left: epitaxial relationships between indium tin oxide substrate and iron oxide (hematite); structural features of crystalline films elucidated at the Advanced Photon Source (Argonne National Lab); measured and calculated pair distribution functions for an active iridium water oxidation catalyst; crystals of a hybrid perovskite material; X-ray crystal structure of a molecular catalyst for proton reduction

IMPACT

- ANSER hosts an annual symposium with the main theme alternating yearly between the two thrusts of the Center (solar electricity and fuels). Each year a roster of six outstanding young and established scientists from the field are invited to discuss their work in a forum open to the community. The symposium is attended by 160+ registered participants from around the Midwest, and is highlighted by a public keynote address from one selected invitee.
- ANSER and the Northwestern University Office for STEM Education Partnership co-host an annual teacher workshop series for middle and high school teachers from the greater Chicago area. The Climate Change and Sustainability Professional Development Series includes workshops, research symposia, lab activities and curriculum development.
- **Catalytic Innovations LLC**, a spin-off company from Yale University founded in 2015 to commercialize molecular materials for catalysis and corrosion resistance. This technology demonstrates an application of research done at ANSER, where Catalytic Innovations' implementation of molecular iridium electrocatalyst technology is the first demonstration of industrial use of a heterogenized molecular catalyst. Catalytic Innovations wastewater systems using this technology are also pioneering solar fuel generation, as an early demonstration of an economically viable solar fuels system. <http://cat.aly.st/>

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, ANSER had published 341 peer-reviewed publications cited over 16,000 times and filed 30 disclosures, 20 US patent applications, and 1 foreign patent applications. One patent has been issued. The following is a selection of impactful papers:

- Stoumpos, C. C., Malliakas, C. D., Kanatzidis, M. G. Semiconducting Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High Mobilities, and Near-Infrared Photoluminescent Properties. *Inorganic Chemistry* **52**, 9019-9038, doi:[10.1021/ic401215x](https://doi.org/10.1021/ic401215x) (2013). [**851 citations**]
- Chung, I., Lee, B., He, J. Q., Chang, R. P. H., Kanatzidis, M. G. All-solid-state dye-sensitized solar cells with high efficiency. *Nature* **485**, 486-U94, doi:[10.1038/nature11067](https://doi.org/10.1038/nature11067) (2012). [**630 citations**]
- Loser, S. *et al.* A Naphthodithiophene-Diketopyrrolopyrrole Donor Molecule for Efficient Solution-Processed Solar Cells. *Journal of the American Chemical Society* **133**, 8142-8145, doi:[10.1021/ja202791n](https://doi.org/10.1021/ja202791n) (2011). [**370 citations**]
- Weingarten, A. S. *et al.* Self-assembling hydrogel scaffolds for photocatalytic hydrogen production. *Nature Chemistry* **6**, 964-970, doi:[10.1038/NCHEM.2075](https://doi.org/10.1038/NCHEM.2075) (2014). [**65 citations**]
- Zhou, N. J. *et al.* Metal-Free Tetrathienoacene Sensitizers for High-Performance Dye-Sensitized Solar Cells. *Journal of the American Chemical Society* **137**, 4414-4423, doi:[10.1021/ja513254z](https://doi.org/10.1021/ja513254z) (2015). [**62 citations**]
- Sheehan, S. W., Thomsen, J. M., Hintermair, U., Crabtree, R. H., Brudvig, G. W., Schmittenmaer, C. A. A molecular catalyst for water oxidation that binds to metal oxide surfaces. *Nature Communications* **6**, 6469, doi:[10.1038/ncomms7469](https://doi.org/10.1038/ncomms7469) (2015). [**48 citations**]

EFRC: FLUID INTERFACE REACTIONS, STRUCTURES AND TRANSPORT (FIRST)

UPDATED: AUGUST 2016

AWARDS: \$19.3M (August 2009 – July 2014); \$15.2M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/EFRC/>; <http://web.ornl.gov/sci/first/>

TEAM: Oak Ridge National Laboratory (Lead): David Wesolowski (Director), Nina Balke, Sheng Dai, Nancy Dudney, Paul Kent, Alexander Kolesnikov, Daniel Lutterman, Shannon Mahurin, Eugene Mamontov, David Mullins, Michael Naguib, Gernot Rother, Robert Sacci, Raymond Unocic, Huiyuan Zhu; **Argonne National Laboratory:** Paul Fenter; **University of California, Davis:** Alexandra Navrotsky; **University of California, Riverside:** De-en Jiang, Jianzhong Wu; **University of Delaware:** Joel Rosenthal; **Drexel University:** Yury Gogotsi; **University of Minnesota:** Matthew Neurock; **The Pennsylvania State University:** Adrianus Van Duin; **Vanderbilt University:** Peter Cummings

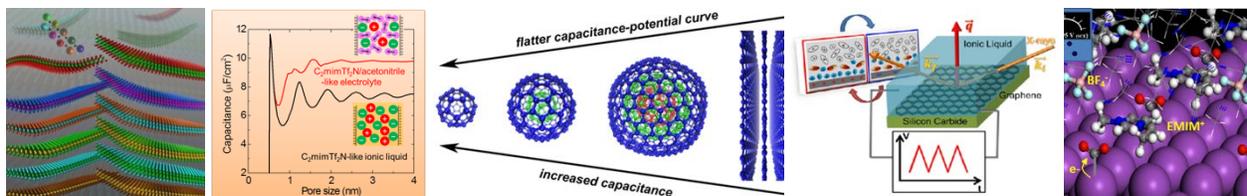
SCIENTIFIC MISSION AND APPROACH

The overarching goal of the FIRST Center is 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 electrocatalysis. FIRST's primary emphasis is on capacitive and pseudocapacitive energy storage controlled by ion sorption and surface redox reactions that occur within the so-called electrical double layer (EDL) at electrode/electrolyte interfaces. The center studies aqueous, organic and room temperature ionic liquid (RTIL) electrolyte solutions and electrode materials including various forms of nanoporous carbon, the novel 2D MXene transition metal carbonitrides and metals. Such interfaces also facilitate electrocatalytic reactions and FIRST seeks to understand the interfacial structures and dynamics that control the mechanisms and efficiency of selected energy-relevant redox reactions. The center consists of two highly interactive Thrusts:

- 1) **Structure and Dynamics of Simple Fluid-Solid Interfaces:** Develop predictive conceptual and multiscale computational models and validate them using advanced nanoscale probes of electrolyte structures, dynamics and reactivity at well-understood interfaces.
- 2) **Structure and Dynamics of Complex Fluid-Solid Interfaces:** Use these models to guide the synthesis of novel materials and functional interfacial systems that address current technological barriers in (pseudo)capacitive electrical energy storage and electrocatalysis.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Developed a deep body of integrated synthesis, computation and nanoscale characterization studies of the structure, dynamics and capacitive energy storage potential of RTILs that is enabling predictive design of supercapacitors that operate at extremes of temperature and electrochemical potential.
- Developed and patented novel electrode materials including onion-like carbons (OLC) with superior rate-handling and sorptive properties for micro- and pseudo-capacitors, and hierarchical ordered mesoporous carbons using a 'bricks and mortar' synthesis approach that enables incorporation of additives like few-layers graphene and OLC to enhance energy and power density and conductivity.
- Used Density Functional Theory (DFT) approaches to predict the stabilities of an entirely new class of conducting 2D mixed-transition-metal carbonitrides (MXenes) and then successfully synthesized several such materials that show great promise for pseudocapacitors and electrocatalysts.
- Combined DFT and reactive classical molecular dynamics simulations to reveal the detailed mechanisms controlling the reduction of CO₂ to CO (a liquid fuel precursor) co-catalyzed by RTIL cations at post-transition metal electrodes, in quantitative agreement with FIRST experiments.



FIRST research, from left: Novel 2D double-transition-metal carbonitrides (MXenes) synthesized based on computational predictions; Classical MD and classical DFT prediction of the oscillatory capacitance of nanoporous electrodes as a function of ion size versus pore size; CMD-predicted effect of surface curvature on nanoparticulate electrode capacitance; novel synchrotron X-ray and neutron scattering and spectroscopic approaches developed to validate computationally-predicted interfacial structures and dynamics; mechanism revealed that controls highly efficient and selective reduction of CO₂ to CO co-catalyzed by imidazolium RTIL cations at a cheap and nontoxic bismuth electrode surface in acetonitrile electrolyte.

IMPACT

- In a series of high impact publications FIRST demonstrated how a new scanning-probe microscopic approach, termed Electrochemical Strain Microscopy (ESM), enables real time monitoring of the rates of ion and electrolyte transport into and out of battery and capacitor electrodes. It works by measuring the local volumetric responses (with submicron lateral resolution) to ion intercalation and pore pressure changes associated with electrode charging/discharging. ESM was licensed to **Asylum Research** and is now available to general users of ORNL's Center for Nanophase Materials Science (CNMS) where it is heavily subscribed. <https://www.asylumresearch.com/>
- FIRST developed and patented the Electrochemical Flow Capacitor (EFC) concept that involves a slurry of micron-sized or larger conducting particles suspended in an aqueous or polar organic electrolyte. The particles become charged by collisions with the current collectors and one another when the slurry is pumped through electrode compartments, storing electrical energy in the EDLs developed in the nanoporous particles and in redox-active sorbed organic molecules. FIRST laid extensive groundwork for establishing the roles of particle size/shape/loading, collector channel size and pseudocapacitive enhancement in controlling performance, and is now developing multiscale computational models to accelerate predictive design. EFC's combine the high power handling and cycle life of supercapacitors with scalable energy storage for grid-scale applications.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, FIRST had published 242 peer-reviewed publications cited over 10,400 times and filed 8 disclosures, 7 US patent applications, and 5 foreign patent applications. 3 patents have been issued and 1 patent application licensed. The following is a selection of impactful papers:

- Balke, N. *et al.* Nanoscale Mapping of Ion Diffusion in a Lithium-Ion Battery Cathode. *Nature Nanotechnology* **5**, 749-754, doi: [10.1038/nnano.2010.174](https://doi.org/10.1038/nnano.2010.174) (2010). [204 citations]
- Feng, G. *et al.* Supercapacitor Capacitance Exhibits Oscillatory Behavior as a Function of Nanopore Size. *Physical Chemistry Letters* **2**, 2859-2864, doi: [10.1021/jz201312e](https://doi.org/10.1021/jz201312e) (2011). [125 citations]
- Mochalin, V. *et al.* The Properties and Applications of Nanodiamonds. *Nature Nanotechnology* **7**, 11-23, doi: [10.1038/NNANO.2011.209](https://doi.org/10.1038/NNANO.2011.209) (2012). [667 citations]
- Pech, D. *et al.* Ultrahigh-Power Micrometre-Sized Supercapacitors Based on Onion-Like Carbon. *Nature Nanotechnology* **5**, 651-654, doi: [10.1038/nnano.2010.162](https://doi.org/10.1038/nnano.2010.162) (2010). [921 citations].
- Simon, P., Gogotsi, Y., Dunn, B. Where do Batteries End and Supercapacitors Begin? *Science* **343**, 1210-1211, doi: [10.1126/science.1249625](https://doi.org/10.1126/science.1249625) (2014). [526 citations]
- Xie, Y. *et al.* Prediction and Characterization of MXene Nanosheet Anodes for Non-Lithium-Ion Batteries. *ACS Nano* **8**, 9606-9615, doi: [10.1021/nn503921j](https://doi.org/10.1021/nn503921j) (2014). [94 citations]
- Zhai, Y. *et al.* Carbon Materials for Chemical Capacitive Energy Storage. *Advanced Materials* **23**, 4828-4850, doi: [10.1002/adma.201100984](https://doi.org/10.1002/adma.201100984) (2011). [943 citations]

EFRC: THE CENTER FOR MOLECULAR ELECTROCATALYSIS (CME)

UPDATED: AUGUST 2016

AWARDS: \$22.5M (August 2009 – July 2014); \$14.0M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/EFRC/>; <http://efrc.pnnl.gov/>

TEAM: Pacific Northwest National Lab (Lead): Morris Bullock (Director), Aaron Appel, Simone Raugai, Michael Mock, Eric Wiedner, Molly O'Hagan; **Yale University:** James Mayer; **University of Illinois:** Sharon Hammes-Schiffer; **University of Wisconsin-Madison:** Shannon Stahl

SCIENTIFIC MISSION AND APPROACH

The vision of the Center for Molecular Electrocatalysis (CME) is to develop a fundamental understanding of proton transfer reactions that will lead to transformational changes in our ability to design molecular electrocatalysts for the interconversion of electricity and fuels. The objective is to *understand, predict, and control* the intramolecular and intermolecular flow of protons in electrocatalytic multi-proton, multi-electron processes including the production of H₂, the oxidation of H₂, the reduction of O₂, and the reduction of N₂. The central hypothesis is that *fast and efficient catalysis* for these reactions *requires control of proton movement over multiple length scales that vary by orders of magnitude*. Through a tightly integrated experimental and theoretical strategy, the CME is identifying the molecular and mesoscale principles required for control of both proton transfer and electron transfer reactions to rationally design fast, efficient molecular electrocatalysts. Three subtasks of the CME efforts are:

- **Production of H₂ and Oxidation of H₂:** Representing the simplest reactions, with only 2 H⁺ and 2 e⁻, the production and oxidation of H₂ are critical for solar fuels production and utilization.
- **Reduction of O₂:** The 4 H⁺ and 4 e⁻ reduction of O₂ to H₂O is the essential reaction in the reductive side of a fuel cell, and represents a substantial increase in complexity relative to H₂.
- **Reduction of N₂ and Oxidation of NH₃:** The reduction of N₂ and oxidation of NH₃ are the most complex of these transformations, involving 6 H⁺ and 6 e⁻, and provide the basis for global food production and a potential energy storage cycle based on nitrogen.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Designed the first molecular electrocatalysts that produce H₂ at a rate (>100,000 s⁻¹) faster than the natural hydrogenase enzyme, albeit at a higher overpotential (lower efficiency). This achievement was only possible through an unprecedented mechanistic understanding and tuning of individual steps of the reaction pathway.
- Designed electrocatalysts for oxidation of H₂ based on iron, an earth-abundant metal that is far less expensive than platinum that is commonly used in fuel cells.
- Designed iron complexes that are very fast electrocatalysts for reduction of oxygen, including the fastest known molecular electrocatalysts. Provided critical understanding of the relationship between rate and overpotential.
- Achieved the lowest overpotential to date for electrochemical O₂ reduction reaction (ORR) with a molecular catalyst system, using cooperative metal-free redox shuttles to mediate chemical and electrochemical reactions. This use of electron- and electron-proton-transfer mediators in molecular electrocatalysis introduces an important new strategy to enhance the energy efficiency and rates of electrochemical reactions.
- First successful example using chromium complexes in the reduction of nitrogen to ammonia, using chromium complexes with specialized polyphosphine ligands.



CME research, from left: Formation of the H-H bond in molecular electrocatalysts involves a transition state that combines H^+ and H ; Chromium has been identified in N_2 reduction studies as offering reactivity unique reactivity compared to molybdenum or tungsten; Control of proton movement is critical in H_2 , O_2 and N_2 reactions; Computational analysis of energetics leads to an understanding of many possible pathways for production of H_2 ; Catalytic oxidation of H_2 can occur by different mechanisms, depending on whether the proton or electron is removed first.

IMPACT

- Control of electron transfers has been studied in energy conversion reactions for decades. Addition or removal of protons are key features, yet few catalysts are designed with the recognition of the critical role of proton movement. The pivotal role of pendant amines functioning as proton relays, pioneered by the CME, has been recognized as a key design principle by many research groups worldwide, using ligands designed in the CME.
- The Hydrogen Catalysis Team (including 12 scientists from the CME) was recognized by the 2015 [ACS Catalysis Lectureship for the Advancement of Catalytic Science](#), marking the first time the lectureship was awarded to a team.
- Used accurate experimental and computational thermodynamic approaches to explore competitive reaction pathways, proving a rational basis for catalyst design that has been adopted by other research groups.
- Many research groups have adopted improved techniques developed in the CME for determining overpotentials (a measure of energy efficiency) for transformations of H_2 , O_2 , CO_2 , and N_2 .
- New computational methodology for calculating the reorganization energy, a key parameter required to calculate the rate, for electron transfer and proton-coupled electron transfer in electrochemical systems, was developed and made freely available to the public by porting to the GAMESS electronic structure program.
- The use of molecular mediators for the O_2 reduction reaction was the subject of a patent application at UW-Madison, where researchers received supplemental funding through the [WARF Accelerator Program](#) to promote commercialization.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, CME had published 122 peer-reviewed publications cited over 4,100 times and filed 1 US patent application. A selection of highly cited papers are:

- Helm, M. L.; Stewart, M. P.; Bullock, R. M.; Rakowski DuBois, M.; DuBois, D. L., A Synthetic Nickel Electrocatalyst with a Turnover Frequency Above $100,000\text{ s}^{-1}$ for H_2 Production. *Science* **333**, 863-866, DOI: [10.1126/science.1205864](https://doi.org/10.1126/science.1205864) (2011). [**423 citations**]
- Warren, J. J.; Tronic, T. A.; Mayer, J. M., Thermochemistry of Proton-Coupled Electron Transfer Reagents and its Implications. *Chemical Reviews* **110**, 6961-7001, DOI: [10.1021/cr100085k](https://doi.org/10.1021/cr100085k) (2010). [**386 citations**]
- Kilgore, U.; et al. $Ni(P^{Ph_2}N^{C_6H_4X_2})_2(BF_4)_2$ Complexes as Electrocatalysts for H_2 Production: Effect of Substituents, Acids, and Water on Catalytic Rates. *Journal of the American Chemical Society* **133**, 5861-5872, DOI: [10.1021/ja109755f](https://doi.org/10.1021/ja109755f) (2011). [**181 citations**]
- DuBois, D. L.; Bullock, R. M., Molecular Electrocatalysts for the Oxidation of Hydrogen and the Production of Hydrogen – The Role of Pendant Amines as Proton Relays. *European Journal of Inorganic Chemistry*, 1017-1027, DOI: [10.1002/ejic.201001081](https://doi.org/10.1002/ejic.201001081) (2011). [**125 citations**]

EFRC: CENTER FOR LIGNOCELLULOSE STRUCTURE AND FORMATION (CLSF)

UPDATED: AUGUST 2016

AWARDS: \$21.0M (August 2009 – July 2014); \$12.5M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/clsf/>; <http://www.lignocellulose.org/>

TEAM: Penn State University (Lead): Daniel J. Cosgrove (Director), Charles Anderson, Ying Gu, Seong H. Kim, Manish Kumar, Janna Maranas, Karl Mueller, B. Tracy Nixon, Ming Tien; **Massachusetts Institute of Technology:** Mei Hong; **North Carolina State Univ.:** Candace Haigler, Yaroslava Yingling; **Oak Ridge National Laboratory:** Hugh O'Neill; **Stony Brook Univ.:** Chang-Jun Liu; **Univ. of Rhode Island:** Alison Roberts; **Univ. of Texas at El Paso:** James Kubicki; **Univ. of Virginia:** Jochen Zimmer

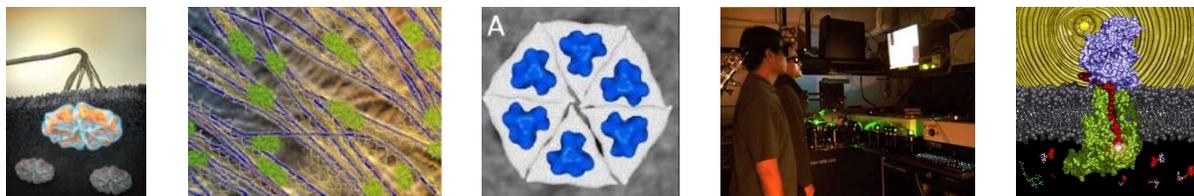
SCIENTIFIC MISSION AND APPROACH

The goals of CLSF are to develop a detailed nano- to meso-scale understanding of plant cell walls, from cellulose microfibril (CMF) formation to the assembly of CMFs with other wall components to form the versatile plant cell wall. Cellulosic biomass (lignocellulose) holds great promise as a large-scale, renewable and sustainable source of liquid biofuels for transportation, if technical obstacles stemming from its complex, hierarchical structure could be overcome. CLSF's research will form the scientific foundation for designing methods to deconstruct cell walls and for coaxing plants into making modified walls for significant advances in sustainable energy and materials. The research is organized around two interconnected themes that lie at the interface of biology and physics:

- 1) **Cellulose Synthesis and Crystallization:** Elucidate how plants synthesize CMFs, including how cellulose synthases (CESAs) polymerize and secrete individual glucan chains and how multimeric cellulose synthase complexes (CSCs) assemble multiple chains into 3-nm-wide CMFs. CMFs are long, crystalline arrays of glucans that form the major load-bearing component of the plant cell wall.
- 2) **Structure and Assembly of Cell Walls:** Elucidate the rules of assembly by which CMFs interact with diverse matrix polymers to form complex, multilamellate structures, ranging from highly extensible primary cell walls in growing tissues to rigid lignified secondary cell walls in xylem and other cells.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Determined the 3D molecular structure for the catalytic domain of a plant CESA. The structure was first proposed based on computational modeling, then confirmed experimentally in a bacterial CESA.
- For the first time, characterized *in-vitro* cellulose biosynthesis in a bacterial cellulose synthesis complex reconstituted from purified components.
- Computationally predicted a deleterious CESA mutation that was then verified through genetic testing and live cell imaging of cellulose synthesis complexes, opening up the possibility of rationally designing CESAs to engineer the properties of cellulose, biomass and biomaterials.
- Discovered that CSC is made from three types of CESAs in equal proportion. Additional experiments and modeling indicate that CSC contains 18 CESAs (3 in each lobe of 6), contrary to the long held assumption that CSC contains 36 CESAs.
- Elucidated the connection between CMF orientation and the cytoskeleton: a protein, CSI1, binds to CESA and microtubules, providing the long-hypothesized link between these two components.
- Developed Sum Frequency Generation Spectroscopy to quantify the amount, orientation, and mesoscale packing of crystalline CMFs in intact plant cell walls. This tool revealed CMFs in secondary cell walls are often aligned in anti-parallel directions.
- Used atomic force microscopy and solid-state NMR to discern direct cellulose-cellulose junctions and cellulose-pectin interactions that dominate primary cell wall structure and its mechanical properties.



CLSF research, from left: Model of cellulose synthesis complex; Model of a primary cell wall: CMF (blue), xyloglucan (green), and pectins (yellow); Experimental evidence for 18 CESAs within the CSC rosette; Yong Bum Park and Chris Lee, CLSF members, utilize sum frequency generation vibration spectroscopy to detect crystalline cellulose in lignocellulosic materials; Afterlife of a Photon – Winner of the 2015 EFRC Poetry of Science Contest (<http://www.energyfrontier.us/content/afterlife-photon>)

IMPACT

- When the CLSF was initiated, a vast communication gap existed between the physical chemists who study cellulose structure and the biologists who are discovering how this material is synthesized by plants. CLSF helped to bridge this gap by organizing and sponsoring two symposia at the American Chemical Society meeting in 2011 and 2012 and a 3-day international symposium at Penn State in 2013 with about 150 attendees.
- Overthrew the “tethered network” model of primary cell walls that dominated the field for the last 25 years. Xyloglucans were postulated to form load-bearing tethers linking dispersed CMFs into a cohesive network, but this was refuted when enzymatic cutting of xyloglucans did not loosen the cell wall. Computational modeling, NMR experiments and atomic force microscopy indicate a cell wall model where strength is controlled at limited, direct junctions formed between CMFs.
- CLSF researchers are recognized as leaders in the cell wall community: they garnered more invitations to speak at the last two international cell wall conferences than any other group.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, CLSF had published 132 peer-reviewed publications cited over 1,600 times and filed one US patent application. A selection of highly cited papers are:

- Park, Y. & Cosgrove, D. A Revised Architecture of Primary Cell Walls Based on Biomechanical Changes Induced by Substrate-Specific Endoglucanases. *Plant Physiology* **158**, 1933-1943, doi:[10.1104/pp.111.192880](https://doi.org/10.1104/pp.111.192880) (2012). **[105 citations]**
- Li, S., Lei, L., Somerville, C. & Gu, Y. Cellulose synthase interactive protein 1 (CSI1) links microtubules and cellulose synthase complexes. *PNAS* **109**, 185-190, doi:[10.1073/pnas.1118560109](https://doi.org/10.1073/pnas.1118560109) (2012). **[97 citations]**
- Wang, T. *et al.* Sensitivity-enhanced solid-state NMR detection of expansin's target in plant cell walls. *Proceedings of the National Academy of Sciences of the United States of America* **110**, 16444-16449, doi:[10.1073/pnas.1316290110](https://doi.org/10.1073/pnas.1316290110) (2013). **[65 citations]**
- Park, Y. & Cosgrove, D. Changes in Cell Wall Biomechanical Properties in the Xyloglucan-Deficient xxt1/xtt2 Mutant of Arabidopsis. *Plant Physiology* **158**, 465-475, doi:[10.1104/pp.111.189779](https://doi.org/10.1104/pp.111.189779) (2012). **[64 citations]**
- Cosgrove, D. J. & Jarvis, M. C. Comparative structure and biomechanics of plant primary and secondary cell walls. *Frontiers in Plant Science* **3**, doi:[10.3389/fpls.2012.00204](https://doi.org/10.3389/fpls.2012.00204) (2012). **[57 citations]**
- Sethaphong, L. *et al.* Tertiary model of a plant cellulose synthase. *Proceedings of the National Academy of Sciences of the United States of America* **110**, 7512-7517, doi:[10.1073/pnas.1301027110](https://doi.org/10.1073/pnas.1301027110) (2013). **[55 citations]**
- Barnette, A. *et al.* Selective Detection of Crystalline Cellulose in Plant Cell Walls with Sum-Frequency-Generation (SFG) Vibration Spectroscopy. *Biomacromolecules* **12**, 2434-2439, doi:[10.1021/bm200518n](https://doi.org/10.1021/bm200518n) (2011). **[43 citations]**
- Omadjela, O. *et al.* BcsA and BcsB form the catalytically active core of bacterial cellulose synthase sufficient for in vitro cellulose synthesis. *Proceedings of the National Academy of Sciences of the United States of America* **110**, 17856-17861, doi:[10.1073/pnas.1314063110](https://doi.org/10.1073/pnas.1314063110) (2013). **[43 citations]**
- Bashline, L. *et al.* The Endocytosis of Cellulose Synthase in Arabidopsis Is Dependent on μ 2, a Clathrin-Mediated Endocytosis Adaptin. *Plant Physiology* **163**, 150-160, doi:[10.1104/pp.113.221234](https://doi.org/10.1104/pp.113.221234) (2013). **[40 citations]**

EFRC: CENTER FOR DIRECT CATALYTIC CONVERSION OF BIOMASS TO BIOFUELS (C3Bio)

UPDATED: AUGUST 2016

AWARDS: \$20.0M (August 2009 – July 2014); \$11.6M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/EFRC/c3bio>; <http://www.purdue.edu/discoverypark/c3bio/>

TEAM: PURDUE UNIVERSITY (Lead): Maureen McCann (Director), Rakesh Agrawal, Nicholas Carpita, Clint Chapple, W. Nicholas Delgass, Hilkka Kenttämä, Richard Meilan, Nathan Mosier, Fabio Ribeiro; **National Renewable Energy Laboratory:** Gregg Beckham, Michael Crowley, Bryon Donohoe, Michael Himmel, Melvin Tucker; **University of California-Santa Barbara:** Mahdi Abu-Omar; **University of Tennessee:** Joseph Bozell; **Northeastern University:** Lee Makowski

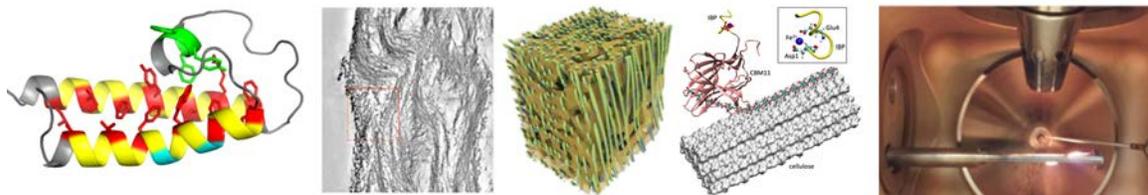
SCIENTIFIC MISSION AND APPROACH

C3Bio explores the potential of chemical catalysis and fast pyrolysis to transform the main components of lignocellulosic biomass (cellulose, xylan, and lignin) from grasses and trees directly to liquid hydrocarbons and aromatic co-products, the components of gasoline and jet fuels. The center aims to specify both the structures within and the reaction products from lignocellulosic biomass. C3Bio's vision is a future of "no carbon left behind"—the full utilization of carbon from plant cell walls in energy-dense fuels and high-value chemicals that are compatible with existing engines and transportation infrastructure. The team of plant biologists, chemists, and chemical engineers address three research goals:

- 1) **Robust catalyses:** Discover catalytic and pyrolytic processes specifically designed for the structural complexity of biomass.
- 2) **Redesigned biomass:** Tailor the structure of plant cell walls to optimize them for carbon- and energy-efficient catalytic and pyrolytic transformations.
- 3) **Biomass-catalyst interactions and systems:** Deliver innovative pathways for targeted product portfolios from tailored lignocellulosic biomass.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Developed a powerful bimetallic catalytic system for the disassembly of lignin via β -O-4 ether bond cleavages from milled wood that produces high-value methoxypropylphenol products. Lignin is the major source of biomass recalcitrance in biochemical conversion processes. The new ability to first deconstruct lignin to useful products revolutionizes the conventional concept of the cellulosic biorefinery in which lignin is a waste stream or co-fired for power generation.
- Built a suite of hydrolysis and catalytic upgrading reactors coupled with in-house, cutting-edge mass-spectrometric analyses to develop a detailed understanding of how fast-hydrolysis and *in situ* hydrodeoxygenation in the presence of appropriate catalyst(s) can produce 100% drop-in hydrocarbon fuels starting from cellulose, methoxypropylphenols, or from delignified biomass. C3Bio found that the number of primary products of fast pyrolysis is greatly reduced, making hydrodeoxygenation in the vapor phase a viable technology.
- Gained genetic control of lignin synthesis within plants to produce poplar trees with high yield and selectivity for a single methoxypropylphenol product after catalytic depolymerization of lignin. This provides proof-of-concept that tailored biomass could reduce energy inputs in the biorefinery, for example, by facilitating product separations.
- New knowledge of the regulatory control of lignin biosynthesis by transcription factors is allowing bypass of a yield penalty commonly observed in plants with modified lignin structures. C3Bio can now simplify lignin structure in plants for downstream conversion without compromising growth.



C3Bio research, from left: crystal structure of a plant-specific domain in cellulose synthase; electron tomogram of a plant cell wall after catalytic treatment; model of secondary wall structure constructed from tomograms; model of a cellulose microfibril bound by a fusion protein delivering an iron catalyst in planta; fast-pyrolysis of cellulose at the inlet of the mass spectrometer.

IMPACT

- C3Bio has organized and/or co-hosted two Frontiers in Bioenergy symposia, three I-cubed workshops for STEM High School teachers, five Duke Energy Academy at Purdue programs, Purdue Bioenergy day, and the Purdue-France Biofuels Workshop together with the French US scientific attaché.
- Maureen McCann leads the Duke Energy Academy at Purdue program (DEAP), a one-week immersive program for High School students and teachers, which aims to inspire pre-college students both to enter STEM disciplines and to envision energy scholarship as part of their educational and career goals. C3Bio faculty contribute lectures, hands-on demonstrations, and research projects for student/teacher teams. Over 400 participants have been supported by a grant from the Duke Energy Foundation in the past five years, and funding is committed through 2019.
- Anchored by C3Bio research, the U.S. Department of the Navy and Purdue University, in 2014, signed a Statement of Cooperation agreeing to work together to convert up to half of the Navy and Marine Corps' energy consumption to alternative sources, including biofuels, by 2020.
- C3Bio's catalytic depolymerization of lignin is the technology basis of start-up company **Spero Energy Inc.**, founded by Mahdi Abu-Omar in 2013 (<http://www.speroenergy.com>). Presently manufactured from petroleum feedstock via a multi-step process, methoxypropylphenols are high-value fragrance and flavor compounds with an annual market value of \$450 M.
- Follow-on funding for C3Bio has exceeded \$6M, including \$1.5M contribution of mass spectrometric equipment from industry partner Thermo Scientific.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, C3Bio had published 119 peer-reviewed publications cited over 2,250 times and filed 18 disclosures, 9 US patent applications, and 3 international patent applications. 4 disclosures or patent applications have been licensed. The following is a selection of impactful papers:

- Bonawitz, N. D., Kim, Y. I., Tobimatsu, Y., Ciesielski, P., Anderson, N. A., Ximenes, E., Maeda, J., Ralph, J., Donohoe, B. S., Ladisch, M. & Chapple, C. Disruption of Mediator rescues the stunted growth of a lignin-deficient *Arabidopsis* mutant. *Nature* **509**, p376–p380, doi: [10.1038/nature13084](https://doi.org/10.1038/nature13084) (2014). [79 citations]
- Parsell, T., Yohe, S., Degenstein, J., Jarrell, T., Klein, I., Gencer, E., Heweston, B., Hurt, M., Kim, J. I., Choudhari, H., Saha, B., Meilan, R., Mosier, N., Ribeiro, F., Delgass, W. N., Chapple, C., Kenttämaa, H. I., Agrawal, R., & Abu-Omar, M. M. A synergistic biorefinery based on catalytic conversion of lignin prior to cellulose starting from lignocellulosic biomass. *Green Chemistry* **17**, p1492-p1499, doi: [10.1039/C4GC01911C](https://doi.org/10.1039/C4GC01911C) (2015). [54 citations]
- Parsell, T. H., Owen, B. C., Klein, I., Jarrell, T. M., Marcum, C. L., Hauptert, L. J., Amundson, L. M., Kenttämaa, H. I., Ribeiro, F. H., Miller, J. T. & Abu-Omar, M. M. Cleavage and hydrodeoxygenation (HDO) of C–O bonds relevant to lignin conversion using Pd/Zn synergistic catalysis. *Chemical Science* **4**, p806-p813, doi: [10.1039/C2SC21657D](https://doi.org/10.1039/C2SC21657D) (2013). [101 citations]
- Ventakrishnan, V. K., Degenstein, J. C., Smeltz, A. D., Delgass, W. N., Agrawal, R. & Ribeiro, F. H. High-pressure fast-pyrolysis, fast-hydroxypropylation and catalytic hydrodeoxygenation of cellulose: production of liquid fuel from biomass. *Green Chemistry* **16**, p792-p802, doi: [10.1039/C3GC41558A](https://doi.org/10.1039/C3GC41558A) (2014). [25 citations]

EFRC: CENTER FOR MESOSCALE TRANSPORT PROPERTIES (*m2m*)

UPDATED: OCTOBER 2016

AWARDS: \$10.4M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/EFRC/>; <http://www.stonybrook.edu/m2m>

TEAM: Stony Brook University (Lead): Esther S. Takeuchi (Director), Amy C. Marschilok (Center Operations Officer), Maria Fernandez-Serra, Kenneth Takeuchi, Stanislaus Wong; **Brookhaven National Laboratory:** Hong Gan, Mark Hybertsen, Ping Liu, Eric Stach, Feng Wang, Jun Wang, Yimei Zhu; **Columbia University:** Alan West; **Georgia Institute of Technology:** Elsa Reichmanis; **University of North Carolina:** Joseph DeSimone; **University of California at Berkeley:** Nitash Balsara; **Oak Ridge National Laboratory:** Nancy Dudney; **Rensselaer Polytechnic Institute:** Robert Hull; **University of Texas at Austin:** Guihua Yu

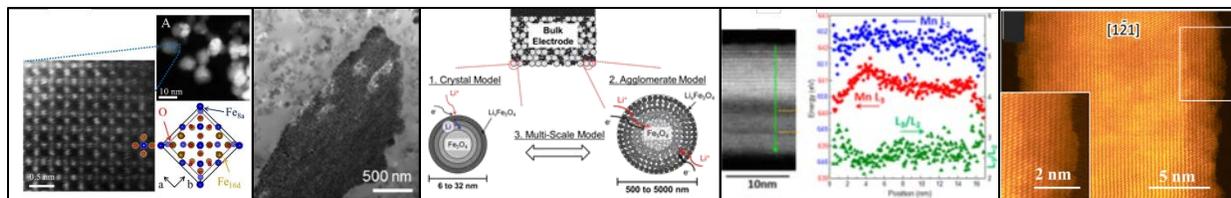
SCIENTIFIC MISSION AND APPROACH

The mission of the Center is to understand and provide control of transport properties in complex battery systems with respect to multiple length scales, from molecular to mesoscale (*m2m*); to minimize heat and maximize work of electrical energy storage devices. While battery inefficiency can be approached at the macro level, emphasizing bulk parameters and bulk methods cannot fully interrogate or address the inherent heterogeneity of ion and electron flux contributing to the local resistance within an electrode and at the interfaces. In order to develop the capability to predict and ultimately control energy storage systems, these inefficiencies must be understood not just as a bulk property (heat), but rather as localized resistance at the molecular to mesoscale (*m2m*) levels. The center has three Scientific Inquiry Areas (SIA):

1. **What are the *fundamental limits* of ion and electron transport and electron transfer over multiple length scales?** Investigation of transport and transfer phenomena for redox active moieties with several configurations and considering the roles of structure, crystallite size and particle size.
2. **How do the phenomena change across *multiple domains* including interfaces?** The influence of physical properties, surface functionalization, and process on the transfer and transport properties and the function of composite electrodes will be explored.
3. **How do the transport phenomena evolve *over time* in systems not at equilibrium?** The effect of extended cycling on energy related solids will be studied to determine the effect of time.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- A comprehensive investigation of multi-electron transfer reactions in Fe₃O₄ was conducted using experiment and *ab-initio* calculations. Results provide the 1st experimental evidence that the cubic-close-packed (ccp) O-anion array in Fe₃O₄ is sustained throughout lithiation and delithiation.
- Detailed analysis of composite electrodes formulated using nanocrystalline Fe₃O₄ quantified the presence of active material aggregates. The first multi-scale mathematical model accounting for mass transport on both the crystal and agglomerate length-scales was developed for magnetite electrodes. Active material utilization predictions due to transport limitations on the material and aggregate size were made possible.
- First direct experimental demonstration of lateral (ab plane) Li⁺ diffusion in 1D α-MnO₂ type materials. Identified possible link with surface oxygen vacancies.
- The formation of a conductive network through a reduction-displacement reaction in Ag_xV_yPO₄ type materials was mapped via EDXRD. The data revealed that a composite electrode formulation is beneficial, but does not ensure complete electrical contact of each active particle.



m2M research, from left: Annual dark-field (ADF) image of a Fe_3O_4 nanoparticles with high-angle ADF image and structural model; Nanocrystalline Fe_3O_4 aggregate TEM image; First predictive multiscale continuum model; STEM-HAADF image of $\text{Ag}_{1.16}\text{Mn}_8\text{O}_{16}$ nanorod. EELS results indicating surface oxygen vacancies; Regenerated $\alpha\text{-MnO}_2$ nanofiber after 100 cycles.

IMPACT

- *m2M* EFRC organized a one-day workshop on Advanced Characterization Techniques for Energy Storage jointly hosted by BNL's Center for Functional Nanomaterials (CFN) and National Synchrotron Light Source-II (NSLS-II). Attendance included other energy storage EFRCs and JCSE. Participated in the Electrochemical Energy Summit at the 228th Electrochemical Society.
- Impact of *m2M* Center noted through 9 invited talks and 5 invited publications including the following. Keynote address at the National Academy of Inventors Induction ceremony in Pasadena, CA. Invited presentation on Contemporary Issues and Case Studies in Electrochemical Innovation 2 at PRIME. Held every four years, this international gathering is the joint effort of The Electrochemical Society (ECS), The Electrochemical Society of Japan (ECSJ), and The Korean Electrochemical Society (KECS).
- *m2M* Director co-authored an invited "Best Practices for Reporting on Energy Storage" editorial for ACS Applied Materials and Interfaces.
- NY state matching funds for the *m2M* EFRC award were obtained to establish a new pouch cell facility for assembly of prototype batteries in the dry room at BNL. This will provide a new institutional resource as a result of the EFRC project.
- *m2M* investigations on Ag^+ and Ag^0 contributions to conductivity led to conceptualization of new program on solid state electrolytes funded by EERE for \$1.2M.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of Oct 2016, *m2M* had published 33 peer-reviewed publications cited over 100 times, filed 2 disclosures and 2 US patent applications. The following is a selection of impactful papers:

- Abraham, A., Housel, L. M., Lininger, C. N., Bock, D. C., Jou, J., Wang, F., West, A. C., Marschilok, A. C., Takeuchi, K. J. & Takeuchi, E. S. Investigating the Complex Chemistry of Functional Energy Storage Systems: The Need for an Integrative, Multiscale (Molecular to Mesoscale) Perspective. *ACS Central Science* **2**, 380-387, doi: [10.1021/acscentsci.6b00100](https://doi.org/10.1021/acscentsci.6b00100) (2016). Invited. [1 citations].
- Dudney, N. J. & Li, J. Using all energy in a battery. *Science* **347**, 131-132, doi: [10.1126/science.aaa2870](https://doi.org/10.1126/science.aaa2870) (2015). [19 citations].
- Zhang, W., Bock, D. C., Pelliccione, C. J., Li, Y., Wu, L., Zhu, Y., Marschilok, A. C., Takeuchi, E. S., Takeuchi, K. J. & Wang, F. Insights into Ionic Transport and Structural Changes in Magnetite during Multiple-Electron Transfer Reactions. *Advanced Energy Materials* **6**, 1502471, doi: [10.1002/aenm.201502471](https://doi.org/10.1002/aenm.201502471) (2016). [3 citations].
- Wu, L., Xu, F., Zhu, Y. *et al.* Structural defects of silver hollandite, $\text{Ag}_x\text{Mn}_8\text{O}_y$, Nanorods: Dramatic impact on electrochemistry. *ACS Nano* **9**, 8430-8439, doi: [10.1021/acsnano.5b03274](https://doi.org/10.1021/acsnano.5b03274) (2015). [10 citations].
- Poyraz, A., Huang, J., Cheng, S. *et al.* Effective Recycling of Manganese Oxide Cathodes for Lithium Based Batteries. *Green Chem.* **18**, 3414-3421, doi: [10.1039/C6GC00438E](https://doi.org/10.1039/C6GC00438E) (2016). [0 citations].
- Bock, D., Pelliccione, C. J., Zhang, W. *et al.* Dispersion of Nanocrystalline Fe_3O_4 Within Composite Electrodes: Insights on Battery Related Electrochemistry, *ACS Appl. Mater. Interfaces* **8**, 11418-11430, doi: [10.1021/acsmi.6b01134](https://doi.org/10.1021/acsmi.6b01134) (2016). [4 citations].

EFRC: CENTER FOR GAS SEPARATIONS RELEVANT TO CLEAN ENERGY TECHNOLOGIES (CGS)

UPDATED: AUGUST 2016

AWARDS: \$10.8M (August 2009 – July 2014); \$12.0M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/cgs/>; <http://www.cchem.berkeley.edu/co2efrc/>

TEAM: University of California, Berkeley (Lead): Jeffrey Long (Director), Jeffrey Neaton, Jeffrey Reimer, Berend Smit (Deputy Director), Ting Xu, Omar Yaghi; **Lawrence Berkeley National Laboratory:** Brett Helms, Jeffrey Kortright, Maciej Haranczyk, David Prendergast, Simon Teat, Steve Whitelam; **National Energy Technology Laboratory:** David Hopkinson; **National Institute of Standards and Technology:** Craig Brown; **Texas A&M:** Hong-Cai Zhou; **University of Minnesota:** Laura Gagliardi, Michael Tsapatsis; **École Polytechnique Fédérale de Lausanne:** Wendy Queen

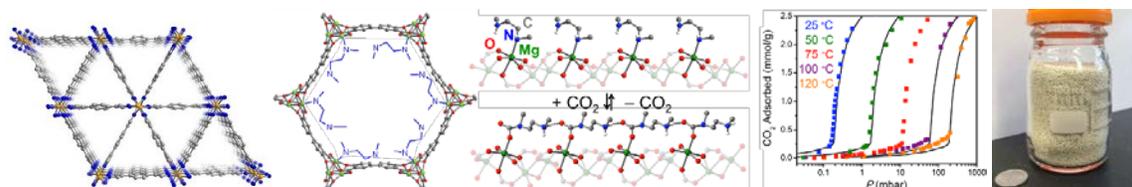
SCIENTIFIC MISSION AND APPROACH

The major aim of CGS is to design and tailor-make new materials for the efficient separation of industrially-relevant gases, which requires the ability to discriminate between their often subtle chemical and physical differences. Thus, CGS is also developing novel characterization and computational methods to guide understanding of the materials properties necessary for such separation specificity and efficiency. Given that industrial separations processes currently account for 10-15% of total global energy consumption, efforts to reduce these energy costs by employing more effective materials represent a vital pursuit towards lowering our overall energy usage. In particular, CGS is targeting novel adsorbents for CO₂ capture, the separation of O₂ from air and N₂ from methane, and for the shape-selective separation of hydrocarbons. CGS research focuses on three major goals:

- 1) **Materials Synthesis:** Design and synthesis of new chemically and mechanically stable adsorbents for more energy-efficient gas separations.
- 2) **Materials Characterization:** Development of novel characterization tools for the rigorous understanding of adsorbent chemical and physical properties, including *in situ* characterization of gas binding in adsorbents via single-crystal X-ray diffraction, X-ray absorption, and nuclear magnetic resonance.
- 3) **Computational Separations:** Creation of novel computational methods to model gas adsorption behavior and to predict as-yet unknown adsorbents with promise in various separations applications.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Discovered a new metal-organic framework (MOF), mmen-Mg₂(dobpdc), that exhibits remarkable CO₂ affinities and capacities arising from an unprecedented cooperative adsorption mechanism that enables material regeneration at much lower temperatures than currently used for amine solvents.
- Developed mixed-matrix (polymer and MOF) membranes that exhibit vastly improved separation of light hydrocarbons and resistance to plasticization relative to the pure polymers.
- Designed novel cobalt-based MOFs that exhibit selective and reversible binding of O₂ over N₂.
- Developed a new computational approach to evaluate a wide range of adsorbents on their performance for capture and storage of CO₂.
- Discovered MOFs that separate hydrocarbon mixtures found in gasoline or natural gas based on pore shape or exposed metal sites, paving the way for a less energy-intensive separation process than cryogenic distillation.
- Designed a highly versatile iron-based MOF that is capable of distinguishing small hydrocarbons as well as efficiently separating O₂ from N₂.



CGS research, from left: triangle channels separate hydrocarbon mixtures based on shape; diamine-appended MOFs can exhibit step-shaped isotherms arising from a new cooperative mechanism for CO₂ adsorption; Mosaic Materials is developing inexpensive methods to make tons of pelletized MOFs.

IMPACT

- Berend Smit and Jeff Reimer co-wrote a book, *Introduction to Carbon Capture and Sequestration*, which they have used to co-teach a University of California, Berkeley course. World Scientific Publishing recently highlighted the book as their best-selling text in energy studies.
- A short film about CGS, co-produced with World Energy TV, was broadcast at the 2016 World Future Energy Summit in Abu Dhabi. The summit is a major meeting for the advancement of clean and sustainable energy and draws over 30,000 attendees from business, academia, and industry. <http://www.cchem.berkeley.edu/co2efrc/resources.html>
- **Mosaic Materials, Inc.**, a start-up company co-founded by Jeffrey Long in June 2014, is working on large-scale synthesis and commercialization of diamine-appended MOFs for CO₂ capture from coal-fired power plants. The mmen-Mg₂(dobpdc) material was brought into an ARPA-E project that used high-throughput screening to identify optimal materials for the low-energy CO₂ capture. In this project, a material was discovered that can adsorb more than 10 weight % CO₂ at 25 °C and release the gas with heating to 80 °C, lowering the energy penalty for carbon capture from 30% for existing technology to an estimated 15% or less. The company is currently incubating within the Cyclotron Road program at Lawrence Berkeley National Laboratory. <http://www.cyclotronroad.org/mosaic/>
- **framergy, Inc.**, a small company started in 2011 to commercialize Hong-Cai Zhou's research, provides high-quality, high-volume MOFs, porous polymer networks, and ligands at low-cost for clean energy and other applications. IP created under CGS-funded research in the Zhou group is being licensed and developed by framergy. <http://www.framergy.com/>
- CGS research accomplishments have been the basis for over \$500K in follow-on funding from ExxonMobil, Ishikawajima-Harima Heavy Industries (IHI), and the California Energy Commission.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, CGS had published 214 peer-reviewed publications cited over 22,200 times, and filed 15 disclosures, 15 US patent applications, and 16 foreign patent applications. One patent has been issued and 12 patent applications licensed. The following is a selection of impactful papers:

- Bachman, J. E. *et al.* Enhanced Ethylene Separation and Plasticization Resistance in Polymer Membranes Incorporating Metal-Organic Framework Nanocrystals. *Nature Materials* **15**, 845-849, doi: [10.1038/nmat4621](https://doi.org/10.1038/nmat4621) (2016). [4 citations]
- McDonald, T. M. *et al.* Cooperative Insertion of CO₂ in Diamine-Appended Metal-Organic Frameworks. *Nature* **519**, 303-308, doi: [10.1038/nature14327](https://doi.org/10.1038/nature14327) (2015). [135 citations]
- Kong, X. *et al.* Mapping of Functional Groups in Metal-Organic Frameworks. *Science* **341**, 882-885, doi: [10.1126/science.1238339](https://doi.org/10.1126/science.1238339) (2013). [95 citations]
- Sumida, K. *et al.* Carbon Dioxide Capture in Metal-Organic Frameworks. *Chemical Reviews* **112**, 724-781, doi: [10.1021/cr2003272](https://doi.org/10.1021/cr2003272) (2012). [2132 citations]
- Lin, L. C. *et al.* *In Silico* Screening of Carbon-Capture Materials. *Nature Materials* **11**, 633-641, doi: [10.1038/nmat3336](https://doi.org/10.1038/nmat3336) (2012). [177 citations]
- Bloch, E. D. *et al.* Hydrocarbon Separations in a Metal-Organic Framework with Open Iron(II) Coordination Sites. *Science* **335**, 1606-1610, doi: [10.1126/science.1217544](https://doi.org/10.1126/science.1217544) (2012). [491 citations]

EFRC: CATALYSIS CENTER FOR ENERGY INNOVATION (CCEI)

UPDATED: AUGUST 2016

AWARDS: \$17.5M (August 2009 – July 2014); \$12.4M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/ccei/>; <http://www.efrc.udel.edu/>

TEAM: University of Delaware (Lead): Dionisios G. Vlachos (Director), Stavros Caratzoulas, Douglas J. Doren, Raul F. Lobo, Basudeb Saha, Stanley I. Sandler, Klaus H. Theopold, Donald A. Watson, Bingjun Xu; **Brookhaven National Laboratory/Yeshiva University:** Anatoly Frenkel; **California Institute of Technology:** Mark E. Davis; **Columbia University/Brookhaven National Laboratory:** Jinguang G. Chen; **Georgia Institute of Technology:** Christopher W. Jones; **Lehigh University:** Mark A. Snyder; **Rutgers University:** Marianthi G. Ierapetritou; **University of Massachusetts Amherst:** Wei Fan, Friederike C. Jentoft; **University of Minnesota:** Paul J. Dauenhauer, J. Ilja Siepmann, Michael Tsapatsis; **University of Pennsylvania:** Raymond J. Gorte, Christopher B. Murray

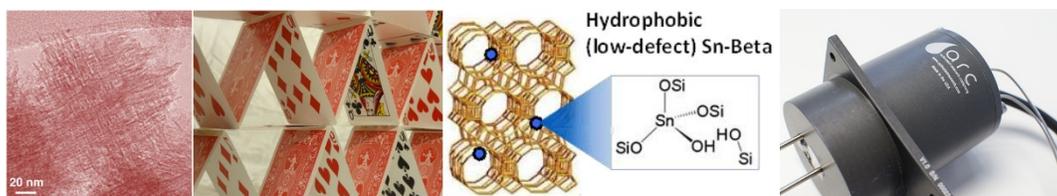
SCIENTIFIC MISSION AND APPROACH

CCEI develops innovative, transformational heterogeneous catalytic technologies for utilization in future biorefineries to economically convert lignocellulosic (non-food-based) biomass into bio-products and fuels. The overarching goals of CCEI are to develop the science that will enable the transformation of lignocellulose to fuels and bio-products, to prepare the workforce for future biorefineries, and to facilitate technology transfer. The center's research consists of three thrusts:

- 1) **Furans:** Efficiently transform sugars (like glucose and xylose) derived from cellulose and hemicellulose biomass to various intermediates, such as furans and fuel-grade compounds.
- 2) **Hydrodeoxygenation (HDO):** Selectively upgrade furans and partially-oxygenated compounds to deoxygenated chemicals and transportation fuels.
- 3) **Aromatics:** Selectively convert and upgrade furans to aromatic compounds (such as BTX – benzene/toluene/xylene), which are important feedstocks in the chemical industry. Existing means of producing BTX are energy-intensive and require petroleum (not shale gas) as a feedstock.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Introduced the first-of-its-kind heterogeneous catalyst (Sn- or Ti-Beta zeolite) for the isomerization of glucose to fructose to replace the existing, costly enzymatic process. Used theory and experiment to explain how these hydrophobic molecular sieves work for glucose and related sugar conversions.
- Demonstrated that the Sn-Beta catalyst is active at low pH and in the presence of salt, enabling tandem reactions to convert glucose to fructose to HMF (a furan that is a potential "carbon-neutral" feedstock for fuels and chemicals) in a single pot. Traditional methods require multiple pots, which can be more costly to implement and generate additional waste.
- Synthesized hierarchical multiscale materials that are hydrothermally stable, possess tunable porosity with bio-inspired functionality in the active sites, and minimized resistance to molecular motion while allowing shape selectivity. The new structures improve the effectiveness of traditional catalysts with no increase in cost or unwanted change in functionality.
- Established the first route for the production of renewable aromatics (BTX, benzoic acid, phthalic anhydride, etc.) from biomass derivatives using acid zeolites on feedstocks from sugars.
- Predicted, and confirmed experimentally, that Mo₂C is an extremely selective deoxygenation catalyst to convert small oxygenates to high demand renewable alkenes, such as propylene.
- Produced the highest yield of dimethylfuran from sugars with an ultra-selective and stable catalyst.



CCEI research, from left: Sheets of zeolite catalysts form an open pore hierarchical structure like a “house-of-cards”; The active site (blue dot) in the Sn-Beta zeolite, surrounded by a hydrophobic sieve, selectively converts sugars derived from biomass; The Polyarc® reactor system is an add-on to gas chromatographs that increases accuracy while eliminating the need for calibration.

IMPACT

- **Activated Research Company (ARC)**, a start-up company founded in 2014, is commercializing the Polyarc® reactor system, an add-on detector to existing gas chromatographs (GCs) that reduces operating costs and improves the accuracy in quantification without the need for calibration standards. GCs are widely used in the petroleum, chemical and other analytical industries. The core technology is based on CCEI work. In June 2016, Wasson-ECE Instrumentation, a leading provider of GCs, partnered with ARC to distribute the Polyarc® reactor system world-wide and incorporate the technology into their own products. <http://www.activatedresearch.com/>
- **Anellotech**, co-founded by George Huber (a CCEI member from 2009-2012) in 2008, is developing cost-competitive renewable chemicals from non-food biomass. These biomass-derived chemicals are used to make important plastics that are used in consumer goods such as beverage bottles, clothing, carpeting, automotive and electronic components. Anellotech, a CCEI industrial partner, has licensed patents which include CCEI-supported investigators as inventors. <http://www.anellotech.com/>
- CCEI’s **Industrial Consortium** accelerates technology transfer by developing long-term relationships with members of industry. Members attend CCEI’s annual meetings, recruit EFRC students and postdocs, and have the option to sponsor research projects that are tailored to the sponsoring company’s interests and needs. Current and past members include: Activated Research Company (ARC), Air-Liquide, Anellotech, Bridgestone Americas Center for Research & Technology, Dow Chemical Company, DuPont Company, ExxonMobil, Renewable Energy Group, INVISTA, Micromidas, Plant PET Technology Collaborative (PTC), The P&G Company, and Virdia. <http://www.efrc.udel.edu/consortium.html>
- CCEI research accomplishments have been the basis for over \$1.1M in follow-on funding from several companies including ExxonMobil, Air Liquide, and PTC (CocaCola, P&G, Nike, Ford, Heinz), \$1.3M from other DOE programs, and at least \$900K from other government agencies.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, CCEI had published 257 peer-reviewed publications cited over 7,500 times and filed 20 disclosures, 16 US patent applications, and 39 foreign patent applications. Six patents have been issued and 5 disclosures or patent applications licensed. A selection of highly cited papers are:

- Moliner, M., Roman-Leshkov, Y. & Davis, M. Tin-containing zeolites are highly active catalysts for the isomerization of glucose in water. *PNAS* **107**, 6164-6168, doi:[10.1073/pnas.1002358107](https://doi.org/10.1073/pnas.1002358107) (2010). [347 citations]
- Yu, W., Porosoff, M. & Chen, J. Review of Pt-Based Bimetallic Catalysis: From Model Surfaces to Supported Catalysts. *Chemical Reviews* **112**, 5780-5817, doi:[10.1021/cr300096b](https://doi.org/10.1021/cr300096b) (2012). [321 citations]
- Nikolla, E. *et al.* "One-Pot" Synthesis of 5-(Hydroxymethyl)furfural from Carbohydrates using Tin-Beta Zeolite. *Acs Catalysis* **1**, 408-410, doi:10.1021/cs2000544 | [10.1021/cs2000544](https://doi.org/10.1021/cs2000544) (2011). [261 citations]
- Roman-Leshkov, Y. *et al.* Mechanism of Glucose Isomerization Using a Solid Lewis Acid Catalyst in Water. *Angewandte Chemie-International Edition* **49**, 8954-8957, doi: [10.1002/anie.201004689](https://doi.org/10.1002/anie.201004689) (2010). [240 citations]
- Carlson, T., Cheng, Y., Jae, J. & Huber, G. Production of green aromatics and olefins by catalytic fast pyrolysis of wood sawdust. *Energy & Environmental Science* **4**, 145-161, doi: [10.1039/c0ee00341g](https://doi.org/10.1039/c0ee00341g) (2011). [194 citations]

EFRC: NANOSTRUCTURES FOR ELECTRICAL ENERGY STORAGE (NEES)

UPDATED: AUGUST 2016

AWARDS: \$14.0M (August 2009 – July 2014); \$11.2M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/nees/>; <http://www.efrc.umd.edu/>

TEAM: University of Maryland, College Park (Lead): Gary Rubloff (Director), Sang Bok Lee, John Cumings, Chunsheng Wang, YuHuang Wang, Liangbing Hu, Janice Reutt-Robey, Bryan Eichhorn; **University of California, Irvine:** Reginald Penner, Zuzanna Siwy, Phil Collins; **Yale University:** Mark Reed; **University of Florida:** Charles Martin; **University of California, Los Angeles:** Bruce Dunn; **University of Utah:** Henry White; **Michigan State University:** Yue Qi; **Sandia National Laboratories:** Kevin Leung, A. Alec Talin, Katherine Jungjohann, Farid El Gabaly

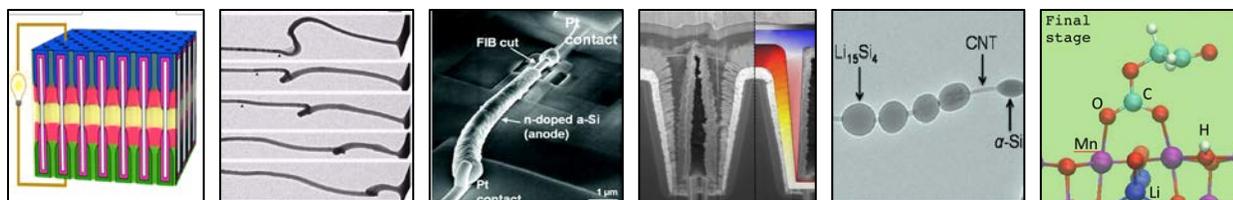
SCIENTIFIC MISSION AND APPROACH

The NEES mission is to reveal scientific insights and design principles that enable a next-generation electrical energy storage technology based on dense mesoscale architectures of multifunctional, heterogeneous nanostructures. Nanotechnology provides the control essential to build such structures and to form them in the highly aggregated, dense arrays to achieve high power and extended cyclability at high energy density. The Center's research is pursued in four thrusts:

- 1) **Transport in Electrochemical Interphases:** To reveal interfacial mechanisms and interphase properties – charge transport, electrochemical reactions and structural changes – and their consequences in battery electrochemistry.
- 2) **Mesoscale Architectures:** To understand ion and electron transport in mesoscale assemblies of storage nanostructures, and to compare performance and cycle stability of architectures assembled in regular and pseudo-random configurations.
- 3) **Nanostructure Degradation Science:** To identify, quantify, & understand key degradation and failure mechanisms that lead to capacity loss with cycling in nanostructured energy storage structures.
- 4) **Solid State Energy Storage:** To directly confront the 3D structure challenges presented by thin film solid electrolyte materials and processes compatible with nanostructure topography and interfaces, and to seek mechanistic insights informed by multiscale modeling.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Pioneered real-time transmission electron microscopy (TEM) to observe lithiation, delithiation, and degradation in single nanowire structures, along with TEM liquid cell for organic electrolytes.
- Identified multi-component nanostructure configurations and chemical mechanisms to stabilize nanoelectrodes against stress-induced degradation associated with ion insertion/deinsertion.
- In both isolated and densely packed nanostructures, demonstrated that high performance storage requires intimately integrated electron and ion transport components, the latter involving length scales less than ~50nm from the electrolyte interface to achieve high power.
- Exploited computational methods (DFT, etc.) to understand degradation and stability at the nanoscale, including electrolyte degradation, formation and mitigation of the solid-electrolyte interphase at electrode surfaces.
- Developed means to enable Li-S batteries – entrapping S in carbon nano/micro structures; thermally modifying polysulfide distributions; using ultrathin protective layers to prevent Li anode degradation.
- Demonstrated first single-nanowire solid state Li ion battery and synthesis of solid electrolytes as needed for advanced 3-D solid state nanobatteries and metal anode protection layers.



NEES research, from left: precision nanostructured batteries; lithiation reaction front observed in TEM; miniature all-solid-state nanowire lithium-ion battery; multiphysics modeling of non-uniform Li^+ transport in all-solid-state Li-ion batteries; a structurally stable silicon-carbon nanotube; a tunable, air-stable electrical conductive metal organic frameworks.

IMPACT

- NEES has led new conceptual research directions based on precision nanostructures as model science platforms, as exemplified by the world's smallest Li ion battery (over 1 million in grain of sand), achieving record-setting capacity retention at high power and cycle stability, demonstrating that ion transport in highly confined electrolyte volumes is not limiting. The work was featured in > 36 media coverage including *The Times* and *National Geographic*, reaching a broad range of public audience.
- NEES has published > 20 invited perspectives and review articles on key scientific concepts involved in using nanostructures and architectures for next generation energy storage.
- In collaboration with DOE Center for Integrated Nanotechnologies (CINT), NEES PIs developed a novel Discovery Platform – a microfabricated sealed liquid cell that allows imaging and control of battery electrochemical processes in an atomic-resolution transmission electron microscope (TEM).
- NEES co-sponsors 2016 CINT Users Meeting Symposium, titled “Electrochemical Nanostructures: Mesoscale Architectures and Integration”, Santa Fe, NM, Sept 2016, highlighting scientific research in nano- materials and structure characterization at the CINT 10 Years of Innovation.
- With K. Xu (ARL), NEES PI C. Wang has co-founded the Center for Research in Extreme Batteries (CREB) to capitalize on battery expertise in NEES, ARL and NIST, promoting open access to facilities and collaborative research in advanced battery materials and technologies.
- Over \$8M follow-on funding from ARPA-E, EERE, NSF and JHU-APL has been awarded to NEES PIs to take nanostructure designs to technology, including the DELTA, RANGE and IDEAS programs in ARPA-E and the CMMI-Nanomanufacturing in NSF.
- **Saft Groupe SA** has been collaborating and supporting NEES PIs, including C. Wang on Li-S and other battery chemistries, and recently G. Rubloff on electrode protection layers. saftbatteries.com

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, NEES had published 187 peer-reviewed publications cited over 8,500 times and filed 12 disclosures, 9 US patent applications, and 1 foreign patent application. 2 patents have been issued. The following is a selection of impactful papers:

- Huang, J. et al. *In Situ* Observation of the Electrochemical Lithiation of a Single SnO_2 Nanowire Electrode. *Science* **330**, p1515-p1520, doi: [10.1126/science.1195628](https://doi.org/10.1126/science.1195628) (2010). [576 citations]
- Guo, J., Xu, Y., Wang, C. Sulfur-Impregnated Disordered Carbon Nanotubes Cathode for Lithium-Sulfur Batteries. *Nano Letters* **11**, p4288-p4294, doi: [10.1021/nl202297p](https://doi.org/10.1021/nl202297p) (2011). [476 citations]
- Liu, R., Duay, J., Lee, S.B. Heterogeneous nanostructured electrode materials for electrochemical energy storage. *Chemical Communications* **47**, p1384-p1404, doi: [10.1039/c0cc03158e](https://doi.org/10.1039/c0cc03158e) (2011). [281 citations]
- Liu, X.H. et al. Anisotropic Swelling and Fracture of Silicon Nanowires during Lithiation. *Nano Letters* **11**, p3312-p3318, doi: [10.1021/nl201684d](https://doi.org/10.1021/nl201684d) (2011). [280 citations]
- Liu, C. et al. An all-in-one nanopore battery array. *Nature Nanotechnology* **9**, p1031-p1039, doi: [10.1038/NNANO.2014.247](https://doi.org/10.1038/NNANO.2014.247) (2014). [39 citations]
- Kozen, A.C. et al. Next-Generation Lithium Metal Anode Engineering via Atomic Layer Deposition. *ACS Nano* **9**, p5884-p5892, doi: [10.1021/acsnano.5b02166](https://doi.org/10.1021/acsnano.5b02166) (2015). [33 citations]

EFRC: CENTER FOR SOLAR FUELS (UNC EFRC)

UPDATED: AUGUST 2016

AWARDS: \$17.5M (August 2009 – July 2014); \$10.8M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/unc/>; www.efrc.unc.edu

TEAM: University of North Carolina at Chapel Hill (Lead): Thomas J. Meyer (Director), Gerald Meyer (Deputy Director), John Papanikolas (Deputy Director), Joanna Atkin, Maurice Brookhart, James Cahoon, Jillian Dempsey, Yosuke Kanai, Rene Lopez, Alex Miller, Andrew Moran, Cynthia Schauer, Joseph Templeton, Kyle Brennaman, Seth Marquard; **University of Texas, San Antonio:** Kirk Schanze; **Georgia Institute of Technology:** John Reynolds; **Brookhaven National Laboratory:** James Muckerman

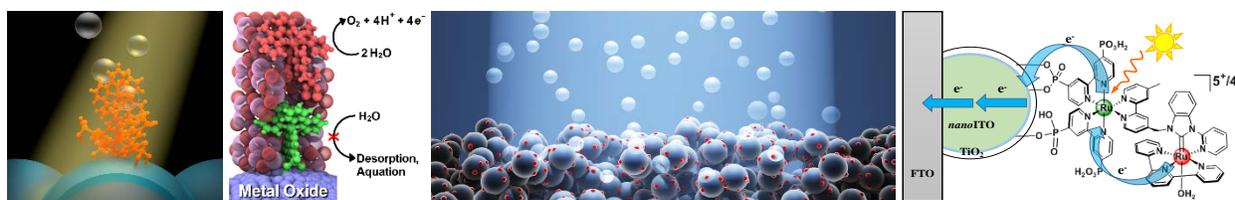
SCIENTIFIC MISSION AND APPROACH

The mission of the UNC EFRC is to conduct research on the dye-sensitized photoelectrosynthesis cell (DSPEC) for water oxidation, and tandem cells for the reduction of carbon dioxide to carbon-based solar fuels for applications in artificial photosynthesis. Research is conducted by five highly integrated teams:

- 1) **Catalysis:** Catalyst development and mechanistic studies on solution and interfacial catalysts for water oxidation and CO₂ reduction.
- 2) **Assemblies:** Design, synthesis, and characterization of molecular and polymer chromophore-catalyst assemblies for applications in water oxidation and CO₂ reduction at *n*- and *p*-type semiconductors.
- 3) **Dynamics:** Develop a detailed understanding of surface mechanisms that guide design of molecular assemblies that improve the performance of photoanodes and photocathodes.
- 4) **Photocathode:** Development of hole-transporting semiconductor nanomaterials and core/shell structures for high-performance photocathodes integrated with catalysts for CO₂ reduction.
- 5) **Photoanode:** Continued optimization of solar-driven water oxidation at dye-sensitized photoanodes.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Successfully pioneered the dye-sensitized photoelectrosynthesis cell (DSPEC) for solar fuels production. DSPECs have been developed for sustained, visible light-driven water splitting with core/shell oxide photoelectrodes derivatized with chromophore-catalyst assemblies.
- New single-site catalysts for water oxidation have been developed, and catalysis has been extended to novel surface-bound assemblies and stable first-row transition metal complexes.
- Rapid, robust catalysts have been developed for CO₂ reduction, including selective reduction of CO₂ either to formate or to tunable H₂/CO (syngas) mixtures, in solution or immobilized on a surface.
- Unique approaches to assemblies have been developed and exploited, including coupling multiple light absorbers with polymer scaffolds to mimic the antenna effect in natural photosynthesis.
- A high degree of surface stabilization has been successfully achieved by atomic layer deposition (ALD) and by electropolymerization, extending surface stabilization from minutes to days.
- Developed a range of chromophore-quencher photoanodes on oxide surfaces for water oxidation with per/photon absorbed efficiencies that approach 1%.
- Photocathode performance was greatly enhanced using targeted atomic deposition (TAD) to eliminate defect states in nanomaterials. Dark saturation current density was decreased by more than one order of magnitude, and device photovoltage was increased by up to 230%.
- Established a world-class spectroscopy facility and, with an integrated theory effort, provided dynamic mapping of key photo-events that occur in assemblies bound to oxide surfaces.



UNC EFRC research, from left: Surface-bound chromophore-catalyst assembly for water oxidation; Stabilization of surface-bound assembly by atomic layer deposition; Artificial photosynthesis in a dye sensitized photoelectrochemical cell; Photoexcitation of chromophore-catalyst assembly on a core/shell photoanode.

IMPACT

- The UNC EFRC hosts an annual international scientific conference in solar fuels, drawing 300-400 participants each year, and funded to-date by \$253K from university and industrial donors.
- UNC EFRC leaders have given 180 invited presentations on energy-related issues to federal and state leaders, universities, industry, and venture capitalists. UNC EFRC researchers have developed and led energy-related outreach programs for schools, teachers, STEM programs, and public science events.
- Support from the UNC EFRC was crucial in creating the new UNC department of Applied Physical Sciences, the first new STEM department in the UNC College of Arts and Sciences in 40 years.
- UNC EFRC research accomplishments have led to \$1.75M in follow-on funding from DOE SciDAC-e and ARPA-E programs, a congressional appropriation for instrumentation, and the Research Triangle Solar Fuels Institute, all of which have augmented the scientific impact of the Center.
- The UNC Solar Energy Research Center (UNC SERC) is leading a translational research effort based on technology developed by the UNC EFRC. Market validation studies have led to a translational effort in CO₂ electroreduction to formic acid for decentralized hydrogen production and storage.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, UNC EFRC had published 233 peer-reviewed publications cited over 10,100 times and filed 27 disclosures, 23 US patent applications, and 17 foreign patent applications. 2 patents have been issued and 2 disclosures or patent applications licensed. The following is a selection of impactful papers:

- Concepcion, J. J. *et al.* Mechanism of Water Oxidation by Single-Site Ruthenium Complex Catalysts. *J. Am. Chem. Soc.* **132**, p1545-p1557, doi:[10.1021/ja904906v](https://doi.org/10.1021/ja904906v) (2010). [247 citations]
- Kang, P. *et al.* Selective Electrocatalytic Reduction of CO₂ to Formate by Water-Stable Iridium Dihydride Pincer Complexes. *J. Am. Chem. Soc.* **134**, p5500-p5503, doi:[10.1021/ja300543s](https://doi.org/10.1021/ja300543s) (2012). [89 citations]
- Ashford, D. L. *et al.* Photoinduced Electron Transfer in a Chromophore-Catalyst Assembly Anchored to TiO₂. *J. Am. Chem. Soc.* **134**, p19189-p19198, doi:[10.1021/ja3084362](https://doi.org/10.1021/ja3084362) (2012). [53 citations]
- Alibabaei, L. *et al.* Solar water splitting in a molecular photoelectrochemical cell. *Proc. Natl. Acad. Sci. USA* **110**, p20008-p20013, doi:[10.1073/pnas.1319628110](https://doi.org/10.1073/pnas.1319628110) (2013). [91 citations]
- Kang, P. *et al.* Single catalyst electrocatalytic reduction of CO₂ in water to H₂ + CO syngas mixtures with water oxidation to O₂. *Energy Environ. Sci.* **7**, p4007-p4012, doi:[10.1039/c4ee01904k](https://doi.org/10.1039/c4ee01904k) (2014). [15 citations]
- Alibabaei, L. *et al.* Visible photoelectrochemical water splitting into H₂ and O₂ in a dye-sensitized photoelectro-synthesis cell. *Proc. Natl. Acad. Sci. USA* **112**, p5899-p5902, doi:[10.1073/pnas.1506111112](https://doi.org/10.1073/pnas.1506111112) (2015). [30 citations]
- Knauf, R. R. *et al.* Charge Recombination Dynamics in Sensitized SnO₂/TiO₂ Core/Shell Photoanodes. *J. Phys. Chem. C* **119**, p28353-p28360, doi:[10.1021/acs.jpcc.5b10574](https://doi.org/10.1021/acs.jpcc.5b10574) (2015). [5 citation]
- Flynn, C. J. *et al.* Site-Selective Passivation of Defects in NiO Solar Photocathodes by Targeted Atomic Deposition. *ACS Appl. Mater. Interfaces* **8**, p4754-p4761, doi:[10.1021/acsami.6b01090](https://doi.org/10.1021/acsami.6b01090) (2016). [4 citations]
- Zigler, D. F. *et al.* Disentangling the Physical Processes Responsible for the Kinetic Complexity in Interfacial Electron Transfer of Excited Ru(II) Polypyridyl Dyes on TiO₂. *J. Am. Chem. Soc.* **138**, p4426-p4438, doi:[10.1021/jacs.5b12996](https://doi.org/10.1021/jacs.5b12996) (2016). [5 citations]
- Leem, G. *et al.* Light-Driven Water Oxidation using Polyelectrolyte Layer-by-Layer Chromophore-Catalyst Assemblies. *ACS Energy Lett.* **1**, p339-p343, doi:[10.1021/acsenergylett.6b00171](https://doi.org/10.1021/acsenergylett.6b00171) (2016). [2 citations]

EFRC: MATERIALS SCIENCE OF ACTINIDES (MSA)

UPDATED: AUGUST 2016

AWARDS: \$18.5M (August 2009 – July 2014); \$11.6M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/msa/>; <http://msa-efrc.com>

TEAM: University of Notre Dame (Lead): Peter C. Burns (Director), Jeremy Fein, Amy Hixon, Edward Maginn; **Stanford University:** Rodney C. Ewing, Wendy Mao; **University of California, Davis:** Alexandra Navrotsky, William H. Casey, Mark Asta; **University of Tennessee:** Maik Lang; **University of Minnesota:** Laura Gagliardi; **University of Akron:** Tianbo Liu; **Oregon State University:** May Nyman; **George Washington University:** Christopher Cahill; **Los Alamos National Laboratory:** Albert Migliori

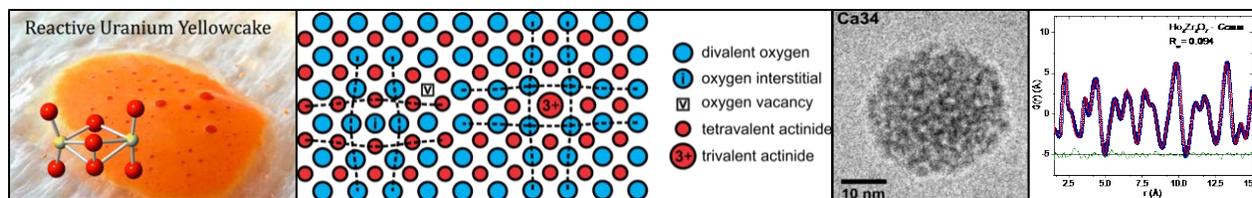
SCIENTIFIC MISSION AND APPROACH

The mission of the MSA is to conduct collaborative, multidisciplinary, novel and transformative research on actinide materials emphasizing actinide ceramic, metallic, hybrid, and nanoscale materials; effectively integrate experimental and computational approaches; and solve research questions that are critical to the energy future of the nation. Workforce development is a fundamental and inherent goal of this university-based center. The center consists of three themes:

- 1) **Nanoscale Cage Clusters:** Develop and understand the unique properties of cage clusters built from actinyl ions to exert nanoscale control of actinide materials.
- 2) **Complex Ceramic and Metallic Materials:** Develop studies of the thermochemistry of actinide materials of importance in the fuel cycle that expand knowledge of actinide chemistry and physics.
- 3) **Materials Under Extreme Environments:** Study the response of actinide materials to combinations of extreme conditions of temperature, pressure, chemical environments, and high-radiation fields.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Developed a family of several dozen self-assembling uranyl cage clusters with diameters from 1.5 to 4.0 nm containing as many as 124 uranium atoms, as well as an understanding of their properties, formation mechanisms, and potential applications in nuclear material processing.
- Energetic radiation can cause dramatic changes in actinide materials, degrading their performance in nuclear energy systems. Advanced synchrotron techniques showed that the redox behavior of the actinide governs radiation tolerance. Limiting the redox activity of actinide materials through control of composition or microstructure can reduce swelling and microstrain.
- In high temperatures or highly ionizing radiation, complex oxides partially lose their crystallinity, which was assumed to occur by a random mixing of their atomic constituents. Neutron scattering experiments revealed that the atoms are not randomly arranged, but only appear so when sampling over longer length scales. Discrepancies may arise when extrapolating the materials structure from the microscale to the atomic scale (or vice versa), which has significant implications for modelling properties and degradation phenomena in actinide materials.
- Uranium dioxide is an important nuclear fuel but it builds up impurities of other oxides as fission products during and after use. A combination of calculations and experimental measurements provided the energetics and structural features of these substitutions, enabling better understanding of the behavior of fuel rods in a reactor and when stored as waste.
- Uranyl peroxide solids and clusters have been shown to be widespread in the nuclear fuel cycle. Their thermodynamic properties have been determined to constrain their formation and decomposition conditions and their potential impact on uranium transport in the environment.



MSA research, from left: reaction of uranium yellowcake with water, releasing O_2 gas, due to compound U_2O_7 ; cation reduction causes structural distortion in the actinide oxide lattice that are identical to that caused by Frenkel defects; cryogenic transmission electron microscope image of a blackberry formed by the aggregation of U_{60} clusters in water; Neutron scattering data revealing the local structure of disordered $Ho_2Zr_2O_7$.

IMPACT

- **Conference Symposia Organized by MSA:** American Chemical Society (ACS) Symposium Fall 2013 (Indianapolis). ACS Symposium Spring 2011 (Anaheim). ACS Symposium Fall 2009 (Washington, D.C.).
- **Selected Awards:** **Ewing:** Roebing Medal of the Mineralogical Society of America, International Mineralogical Association Medal. **Burns:** Peacock Medal of the Mineralogical Association of Canada. **Navrotsky:** American Ceramic Society Kingery Medal, Geochemical Society Goldschmidt Medal. **Migliori:** Joseph F. Keithley Award for Advances in Measurement Science. **Casey:** Geochemical Society Patterson Medal.
- EFRC research concerning pressurization of drums of uranium yellowcake revealed the presence of an amorphous and reactive uranium peroxide that was structurally characterized. This material may release oxygen gas, potentially causing pressurization of drums of yellowcake during storage or transport that could cause an accident. This research has been used by **Uranium One** to prevent accidents involving rapid depressurization of yellowcake drums. <http://www.uranium1.com/>

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, MSA had published 272 peer-reviewed publications cited over 4,200 times and filed 4 disclosures and 4 US patent applications. The following is a selection of impactful papers:

- Burns, P.C., Ewing, R.C., Navrotsky, A. Nuclear fuel in a reactor accident. *Science* **335**, 1184-1188, DOI:[10.1126/science.1211285](https://doi.org/10.1126/science.1211285) (2012). [101 citations]
- Qiu, J., Burns, P.C. Clusters of actinides with oxide, peroxide, or hydroxide bridges. *Chemical Reviews* **113**, 1097-1120, DOI:[10.1021/cr300159x](https://doi.org/10.1021/cr300159x) (2013). [82 citations]
- Tracy, C.L. *et al.* Redox response of actinide materials to highly ionizing radiation. *Nature Communication* **6**, 6133, DOI:[10.1038/ncomms7133](https://doi.org/10.1038/ncomms7133) (2015). [12 citations]
- Vlasisavljevich, B., Gagliardi, L., Burns, P.C. Understanding the structure and formation of uranyl peroxide nanoclusters by quantum chemical calculations. *Journal of the American Chemical Society* **132**, 14503-14508, DOI:[10.1021/ja104964x](https://doi.org/10.1021/ja104964x) (2010). [63 citations]
- Shamblin, J. *et al.* Probing disorder in isometric pyrochlore and related complex oxides. *Nature Materials* **15**, 507-511, DOI:[10.1038/nmat4581](https://doi.org/10.1038/nmat4581) (2016). [8 citation]
- Lang, M. *et al.* Characterization of ion-induced radiation effects in nuclear materials using synchrotron X-ray techniques. *Journal of Materials Research* **40**, 1366-1379, DOI:[10.1557/jmr.2015.6](https://doi.org/10.1557/jmr.2015.6) (2015). [3 citation]
- Guo *et al.* Thermodynamics of formation of coffinite. *Proceedings of the National Academy of Sciences of the United States of America* **112**, 6551-6555, DOI:[10.1073/pnas.1507441112](https://doi.org/10.1073/pnas.1507441112) (2015). [12 citations]
- Odoh, S.O. *et al.* Structure and reactivity of X-ray amorphous uranyl peroxide, U_2O_7 . *Inorganic Chemistry* **55**, 3541-3546, DOI:[10.1021/acs.inorgchem.6b00017](https://doi.org/10.1021/acs.inorgchem.6b00017) (2016). [3 citation]
- Rai, N. *et al.* Force field development for actinyl ions via quantum mechanical calculations: An approach to account for many body solvation effects. *Journal of Physical Chemistry B* **116**, 10885-10897, DOI:[10.1021/jp3028275](https://doi.org/10.1021/jp3028275) (2012). [19 citations]
- Wang, S. *et al.* NDTB-1: A supertetrahedral cationic framework that removes TcO_4^- from solution. *Angewandte Chemie International Edition* **49**, 1057-1060, DOI:[10.1002/anie.200906397](https://doi.org/10.1002/anie.200906397) (2010). [87 citations]

EFRC: CENTER FOR FRONTIERS OF SUBSURFACE ENERGY SECURITY (CFSES)

UPDATED: AUGUST 2016

AWARDS: \$15.5M (August 2009 – July 2014); \$11.2M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/EFRC/>; <http://www.utefrc.org/>

TEAM: The University of Texas at Austin (Lead): Larry W. Lake (Director), Hilary Olson, Tip Meckel, Matthew Balhoff, M. Bayani Cardenas, David DiCarlo, Nicolas Espinoza, Nick Hayman, Marc Hesse, Susan Hovorka, Keith Johnston, Masa Prodanovic, Mary F. Wheeler, Changbing Yang;

Sandia National Laboratories: Grant Heffelfinger, Susan Altman, Thomas Dewers, Mario Martinez, Anastasia Ilgen, Pania Newell, Hongkyu Yoon

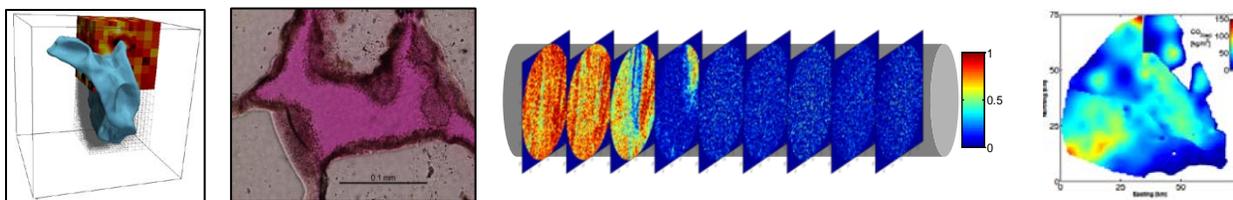
SCIENTIFIC MISSION AND APPROACH

The mission of CFSES is to understand and control emergent (unexpected) behavior arising from coupled physics and chemistry in heterogeneous geomaterials, particularly during the years to decades time scales. The research is tackling three technical challenges: sustaining large storage rates, using pore space with unprecedented efficiency, and controlling undesired or unexpected behavior in geostorage. CFSES is organized into two themes:

- 1) **Fluid-Assisted Geomechanics:** Through investigations of the surface-controllable variables of pore pressure, injectate chemistry, and behavior of subsurface heterogeneity, the research efforts focus on coupled hydro-mechano-chemical processes that address the GCS challenges of storage efficiency, sustaining injection rates, and avoidance of emergent, unwanted behaviors.
- 2) **Buoyancy-Driven Multiphase Flow:** Uses an aligned combination of field observation, laboratory experimentation and model development aimed at understanding and exposing emergent patterns and control strategies for multiphase flow in heterogeneous geomaterials.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Developed numerical models that describe the size and shape of fractures caused by arbitrary stimulation and loading. Based on a novel phase field approach and when coupled with injectate chemistry, the models estimate the likelihood of a breach in the confining layer(s) of a storage site.
- Used invasion percolation modeling (a different type of model from above) of buoyant and capillary forces to analyze and predict the storage efficiency of CO₂ trapping at a given site. The work relates immobilization of CO₂ to traditional geologic characteristics of grain size and grain sorting. The method developed becomes one of several that can screen candidate storage sites.
- Used the Bravo Dome CO₂ field in New Mexico as a natural laboratory to understand the CO₂ behavior in the subsurface. Averaged across the reservoir, only 20% of the CO₂ had dissolved into the field's saline brine over 1.2 million years. The rest remained as a free gas trapped by the cap-rock. This study was the first field evidence for the safe long-term storage of very large amounts of CO₂ in saline aquifers.
- Developed and experimentally validated models that can predict the growth of a single fracture in the presence of subsurface stress and reactive water. This model should enable the anticipation and prevention of unwanted fracturing and the ability to control the fracture pathway.
- Showed that injecting surface-treated nanoparticles into heterogeneous reservoirs causes more uniform CO₂ spreading than without them, thereby increasing CO₂ storage efficiency by as much as 30%.



CFSES research, from left: Phase-field model of propagating fracture in a three dimensional heterogeneous media; Photomicrograph showing diffuse chlorite grain boundary after exposure to CO₂ (pink is the pore space between the grains); X-Ray computerized tomographic image of a core showing the uniform flow of CO₂ with surface-treated nanoparticles through a sandstone core; Distribution of dissolved CO₂ in the subsurface at Bravo Dome natural analog site.

IMPACT

- CFSES collaboration resulted in two successful National Energy Technology Laboratory (NETL) grants totaling over \$2.5M. One project is on the geomechanics of CO₂ reservoir seals and the other on a nanoparticle injection technology for remediating CO₂ storage.
- CFSES collaboration resulted in funding of a Sandia-University of Texas Academic Alliance grant on induced seismicity in CO₂ reservoirs. This project is closely aligned and integrated with induced seismicity research funded by the State of Texas through a \$4.5 million project to build a statewide earthquake monitoring system in Texas and to conduct earthquake research.
- Researchers have an ongoing applied research project stemming from the CFSES research on surface-treated nanoparticles. An oil production company is planning a pilot project where the nanoparticles that help control the movement of CO₂ in the subsurface will be co-injected at an oil reservoir with CO₂ for enhanced oil recovery.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, CFSES had published 107 peer-reviewed publications cited over 900 times and filed 3 disclosures and one US patent application. One patent has been issued. The following is a selection of impactful papers:

- Cygan, R. T., Romanov, V. N. and Myshakin, E. M. Molecular Simulation of Carbon Dioxide Capture by Montmorillonite Using an Accurate and Flexible Force Field. *Journal of Physical Chemistry C* **116**, 13079-13091, doi:[10.1021/jp3007574](https://doi.org/10.1021/jp3007574) (2012). [50 citations]
- Yoon, H., Valocchi, A. J., Werth, C. J. and Dewers, T. Pore-scale simulation of mixing-induced calcium carbonate precipitation and dissolution in a microfluidic pore network. *Water Resources Research* **48**, doi:[10.1029/2011wr011192](https://doi.org/10.1029/2011wr011192) (2012). [31 citations]
- Zhang, Y. P. *et al.* Hydrogeologic Controls on Induced Seismicity in Crystalline Basement Rocks Due to Fluid Injection into Basal Reservoirs. *Ground Water* **51**, 525-538, doi:[10.1111/gwat.12071](https://doi.org/10.1111/gwat.12071) (2013). [31 citations]
- Chaudhary, K. *et al.* Pore-scale trapping of supercritical CO₂ and the role of grain wettability and shape. *Geophysical Research Letters* **40**, 3878-3882, doi:[10.1002/grl.50658](https://doi.org/10.1002/grl.50658) (2013). [28 citations]
- Worthen, A. J. *et al.* Nanoparticle-stabilized carbon dioxide-in-water foams with fine texture. *Journal of Colloid and Interface Science* **391**, 142-151, doi:[10.1016/j.jcis.2012.09.043](https://doi.org/10.1016/j.jcis.2012.09.043) (2013). [29 citations]
- Altman, S. J. *et al.* Chemical and Hydrodynamic Mechanisms for Long-Term Geological Carbon Storage. *Journal of Physical Chemistry C* **118**, 15103-15113, doi:[10.1021/jp5006764](https://doi.org/10.1021/jp5006764) (2014) [10 citations]
- Sathaye, K. J., Hesse, M. A., Cassidy, M. and Stockli, D. F. Constraints on the magnitude and rate of CO₂ dissolution at Bravo Dome natural gas field. *Proceedings of the National Academy of Sciences of the United States of America* **111**, 15332-15337, doi:[10.1073/pnas.1406076111](https://doi.org/10.1073/pnas.1406076111) (2014). [11 citations]
- Rinehart, A. J., Dewers, T., Broome, S. T. and Eichhubl, P. Effects of CO₂ on mechanical variability and constitutive behavior of the Lower Tuscaloosa Formation, Cranfield Injection Site, USA. *International Journal of Greenhouse Gas Control* **53**, 305-318, doi:[10.1016/j.ijggc.2016.08.013](https://doi.org/10.1016/j.ijggc.2016.08.013) (2016). [0 citations]

EFRC: PHOTOSYNTHETIC ANTENNA RESEARCH CENTER (PARC)

UPDATED: AUGUST 2016

AWARDS: \$20.0M (August 2009 – July 2014); \$14.4M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/parc/>; <http://parc.wustl.edu/>

TEAM: **Washington University in St. Louis (Lead):** Robert Blankenship (Director), Dewey Holten (Associate Director), Himadri Pakrasi, Christine Kirmaier, Michael Gross; **Los Alamos National Laboratory:** Gabriel Montaño; **North Carolina State University:** Jonathan Lindsey; **Northwestern University:** Paul Loach, Pamela Parkes-Loach; **Oak Ridge National Laboratory:** Dean Myles, Volker Urban; **Princeton University:** Gregory Scholes; **Sandia National Laboratories:** Jerilyn Timlin; **The Pennsylvania State University:** Donald Bryant; **University of California-Riverside:** David Bocian; **University of Glasgow (UK):** Richard Cogdell; **University of Illinois at Urbana-Champaign:** Klaus Schulten; **University of New Mexico:** Andrew Shreve; **University of Pennsylvania:** P. Leslie Dutton, Christopher Moser; **University of Sheffield (UK):** C. Neil Hunter

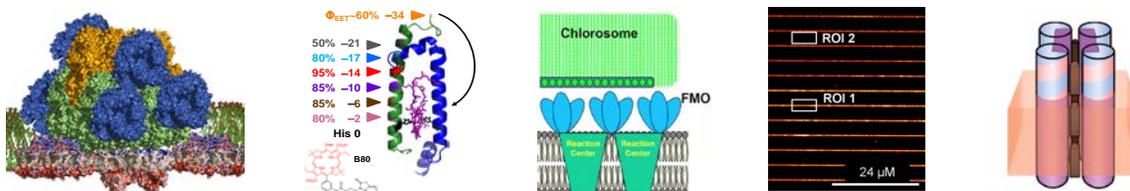
SCIENTIFIC MISSION AND APPROACH

PARC is dedicated to understanding the basic scientific principles that underpin the efficient functioning of natural photosynthetic antenna systems as a basis for design of biohybrid and bioinspired architectures for next-generation systems for solar-energy conversion. Through basic scientific research, PARC seeks to understand the principles of light harvesting and energy funneling. The center has three scientific themes:

- 1) **Natural Antennas: Structure and Efficiency** – To determine and manipulate the antenna architecture and composition to maximize photosynthetic efficiency and functionality in any such organism.
- 2) **Biohybrid and Bioinspired Antennas: Design and Characterization** – To design biohybrid and bioinspired architectures for energy collection and storage.
- 3) **Antenna-Reaction Center Interface: Organization and Delivery** – To understand and control the coupling of antenna and reaction center functions in solar energy conversion systems.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Discovered and characterized a megacomplex in oxygenic photosynthetic cyanobacteria consisting of Photosystems I and II and the large phycobilisome antenna complex using chemical cross-linking and mass spectrometry.
- Melded tunable synthetic chromophores, native bacteriochlorophyll and scaffolding provided by native or native-like α and β peptides from photosynthetic bacteria to develop versatile biohybrid antennas that expand the light-harvesting capacity over native systems.
- The role of red-shifted pigments in increasing photosynthetic efficiency has been investigated and the biosynthetic pathway of the most red-shifted chlorophyll, chlorophyll *f*, has been elucidated.
- Synthetic biology has been utilized to engineer a yellow fluorescence protein into a bacterial photosystem. Studies spanning isolated complexes to whole cells reveals that the introduced protein affords 50% energy transfer efficiency to the native phototrap and augments photosynthetic growth.
- Novel surface nanostructures have been nanopatterned from native, biohybrid and artificial components and characterized by cutting-edge microscopy. The results open the door to achieving efficient, directional energy and charge flow over meso-scale distances.



PARC research, from left: Fig. 1. Structural model of the cyanobacterial megacomplex. Fig. 2. Biohybrid antennas with native bacterial peptides and synthetic chromophores. Fig. 3. Mass-spectrometry based footprinting tests two models for Fenna-Matthews-Olson protein. Fig. 4. Nanopatterned LHClI complexes. Fig. 5. Synthetic maquette 4-helix pigment-protein complexes.

IMPACT

- Provided fundamental insights into native, biohybrid and synthetic antennas driving future research.
- Promoted the use of synthetic biology to confer new capabilities on photosynthetic organisms, such as engineering a bacterial species to utilize multiple biosynthesis pathways to synthesize alternative carotenoids to probe light-harvesting and photoprotection functions.
- Developed/implemented antenna fabrication and characterization tools that foster detailed insight into structure and function of light-harvesting architectures. These include chemical cross-linking, mass spectrometry, hyperspectral imaging, neutron scattering, nanopatterning and advanced microscopy. These methods have been highly cited and adopted by numerous other research groups.
- Significant outreach efforts through PARC lead Saturday Hot Topics Workshops, Summer Workshop Series, tours, and the availability of PARC-developed energy kits and materials have reached >5500 K-12 students and 230 teachers. PARC's Science in St. Louis Seminar Series at local libraries, designed to connect people with scientists in the community, have been attended by 900 public community members (513 adults, 387 students) with 1400 hits on PARC and Science in St. Louis Youtube sites.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, PARC had published 174 peer-reviewed publications cited over 2,100 times. The following is a selection of impactful papers:

- Liu, H., Zhang, H., Niedzwiedzki, D. M., Prado, M., He, G., Gross, M. L. and Blankenship, R. E. Phycobilisomes supply excitations to both photosystems in a megacomplex in cyanobacteria. *Science* **342**, 1104-1107, doi: [10.1126/science.1242321](https://doi.org/10.1126/science.1242321), (2013). [**84 citations**]
- Harris, M. A., Jiang, J., Niedzwiedzki, D.M., Jiao, J., Taniguchi, M., Kirmaier, C., Loach, P.A., Bocian, D.F., Lindsey, J.S., Holten, D., and Parkes-Loach, P.S. Versatile Design of Biohybrid Light-Harvesting Architectures to Tune Location, Density and Spectral Coverage of Attached Synthetic Chromophores for Enhanced Energy Capture, *Photosynthesis Research* **121**, 35–48, doi: [10.1007/s11120-014-9993-8](https://doi.org/10.1007/s11120-014-9993-8), (2014). [**6 citations**]
- Vasilev, C., Johnson, M. P., Gonzales, E., Wang, L., Ruban, A. V., Montaño, G., Cadby, A. J., and Hunter, C. N. Reversible Switching between Nonquenched and Quenched States in Nanoscale Linear Arrays of Plant Light-Harvesting Antenna Complexes. *Langmuir* **30**, 8491-8490, doi: [10.1021/la501483s](https://doi.org/10.1021/la501483s), (2014). [**3 citations**]
- Goparaju, G., Fry, B. A., Chobot, S. E., Wiedman, G., Moser, C. C., Dutton, P. L., Discher, B. First principles design of a core bioenergetic transmembrane electron transfer protein. *Biochimica et Biophysica Acta* **1857**, 503-512, doi: [10.1016/j.bbabi.2015.12.002](https://doi.org/10.1016/j.bbabi.2015.12.002), (2016). [**2 citations**]
- Collins, A.M., Liberton, M., Garcia, O.F., Jones, H.D.T., Pakrasi, H.B. and Timlin, J.A. Photosynthetic pigment localization and thylakoid membrane morphology are altered in *Synechocystis* 6803 phycobilisome mutants. *Plant Physiology* **158**:1600-1609, doi: [10.1104/pp.111.192849](https://doi.org/10.1104/pp.111.192849), (2012). [**25 citations**]
- Orf, G. S., Saer, R., McIntosh, C.L., Zhang, H., Niedzwiedzki, D.M. and Blankenship, R.E. Reactive cysteine residues gate energy transfer in the FMO complex from *Chlorobaculum tepidum*. *Proc. Nat'l. Acad. Sci. USA*, doi: [10.1073/pnas.1603330113](https://doi.org/10.1073/pnas.1603330113), (2016). [**1 citation**]
- Ho, M.-Y., Shen, G., Canniffe, D. P., Zhao, C. and Bryant, D. A. Light-dependent chlorophyll *f* synthase is a highly divergent paralog of PsbA of photosystem II. *Science* **353**, 886. doi: [10.1126/science.aaf9178](https://doi.org/10.1126/science.aaf9178) (2016) [**2 citations**]

FRONT COVER IMAGE

Air bubbles in a mixture of liquid water and Oleo-Furan-Surfactant (OFS) soap made with fatty acids from soybeans or coconut and sugar-derived rings from corn. Researchers from the Catalysis Center for Energy Innovation, an EFRC led by Dionisios Vlachos at the University of Delaware (page 41), have invented a new soap molecule made from renewable sources that could dramatically reduce the number of chemicals in cleaning products and their impact on the environment. The soap molecules also worked better than some conventional soaps in challenging conditions such as cold water and hard water. The technology has been patented by the University of Minnesota and is licensed to the new Minnesota-based startup company Sironix Renewables.

Image courtesy of the Catalysis Center for Energy Innovation (CCEI) EFRC.

NUMBER OF CITATIONS

The journal Time Cited counts were taken from the Web of Science™ Core Collection on January 12, 2017.

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