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INTRODUCTION TO THE GRADUATE STUDENT AND POSTDOCTORAL RESEARCHER COMPETITION AT THE 2013 EFRC PRINCIPAL INVESTIGATORS' MEETING

The EFRC Program

The Energy Frontier Research Centers (EFRC) represent a unique approach to energy research, bringing together the skills and talents of teams of investigators to perform energy-relevant, basic research with a scope and complexity beyond that possible in typical single-investigator or small group research projects. The EFRCs have world-class teams of researchers, often from multiple institutions, bringing together leading scientists from universities, national laboratories, nonprofit organizations, and for-profit firms. The Centers were selected in 2009 by scientific peer review and funded at $2-5 million per year for a 5-year initial award period, subject to Congressional appropriations. These integrated, multi-investigator Centers are tackling some of the toughest scientific challenges hampering advances in energy technologies.

EFRC Research Areas

The 46 EFRC awards span the full range of energy research challenges described in the Basic Energy Sciences series of workshop reports (see http://science.energy.gov/bes/news-and-resources/reports/) in which the community defined basic research that is needed to enable advances related to clean energy technologies, including: solar energy utilization, clean and efficient combustion, electrical energy storage, carbon capture and sequestration, advanced nuclear systems, catalysis, materials in extreme environments, hydrogen science, solid state lighting, and superconductivity. The EFRCs also address scientific grand challenges described in the report, Directing Matter and Energy: Five Challenges for Science and the Imagination.

The EFRCs provide an important bridge between basic research and energy technologies and complement other research activities funded by the Department of Energy. EFRCs accelerate energy science by providing an environment that encourages high-risk, high-reward research that would not be done otherwise; integrating synthesis, characterization, theory, and computation to accelerate the rate of scientific progress; developing new, innovative experimental and theoretical tools that illuminate fundamental processes in unprecedented detail; and training an enthusiastic, inter-disciplinary community of energy-focused scientists.

Graduate Student and Postdoctoral Researcher Competition at the 2013 EFRC Principal Investigators' Meeting

From the more than 1800 graduate students and postdoctoral researchers involved in the EFRC program, each of the 46 EFRCs was invited to nominate one graduate student and one postdoctoral researcher to present a talk at the 2013 EFRC Principal Investigators' Meeting. The DOE EFRC management team then selected 22 finalists to present a talk at the EFRC Principal Investigators' Meeting in Washington, D.C. on July 18 – 19, 2013. At the meeting, teams of DOE program managers selected the top three graduate students and postdoctoral researchers based on how well the research exemplified the opportunities provided by the EFRC funding modality and scientific excellence. The winners received an award certificate from Harriet Kung, Associate Director of the DOE Office of Basic Energy Sciences, during a ceremony at the end of the meeting.

GRADUATE STUDENT WINNERS

PREVENTING HELIUM-INDUCED DAMAGE THROUGH INTERFACE ENGINEERING

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He implanted into metals precipitates into nanoscale bubbles that may later grow into voids, degrading the properties of engineering alloys in nuclear energy applications. However, using multiscale modeling, we find that at fcc-bcc interfaces, He is initially trapped in the form of stable, sub-nanometer platelet-shaped clusters, not bubbles[1]. This behavior occurs due to the spatial heterogeneity of the interface energy (Figure 1): He wets high energy, “heliophilic” regions while avoiding low energy, “heliophobic” ones. This insight allows us to predict the maximum He concentration that can be stored without forming bubbles at any interface in terms of its location-dependent energy distribution. We confirmed our modeling predictions with neutron reflectometry measurements, which showed that interfacial He bubbles form only above a critical He concentration and provided evidence for the presence of stable He platelets below the critical He concentration. Our work paves the way for the design of composite structural materials with increased resistance to He-induced degradation by tailoring the types of interfaces they contain. Such materials are indispensible for advanced fission and future fusion reactors.

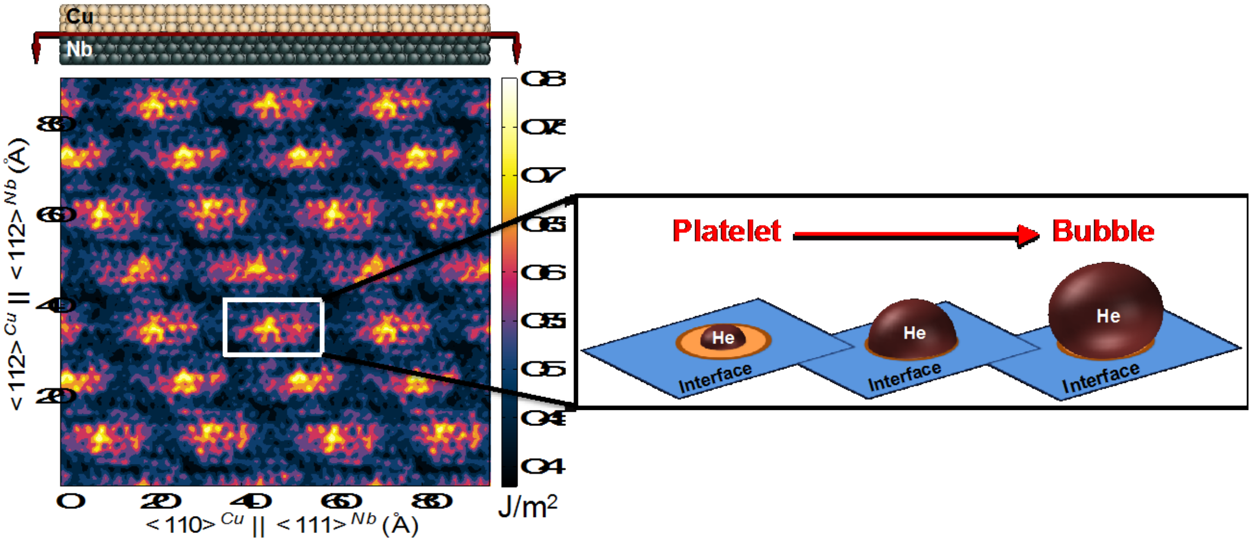

Figure 1. (left) Location dependence of Cu-Nb interface energy looking normal to the interface plane. Patches of highest energy are “heliophilic.” (right) Schematic showing the growth of a He platelet and its eventual transformation into a bubble upon exhausting the “heliophillic” interface patch.

References:

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COHERENT PHONON HEAT CONDUCTION IN SUPERLATTICES

[S3TEC] Maria N. Luckyanova[1]; Jivtesh Garg[1]; Keivan Esfarjani[1]; Adam Jandl[2]; Zhiting Tian[1]; Bo Qiu[1]; Mayank T. Bulsara[2]; Aaron J. Schmidt[3]; Austin J. Minnich[4]; Shuo Chen[5]; Mildred S. Dresselhaus[6]; Zhifeng Ren[5]; Eugene A. Fitzgerald[2]; Gang Chen[1]
[1]Department of Mechanical Engineering, MIT; [2]Department of Materials Science and Engineering, MIT; [3]Department of Mechanical Engineering, Boston University; [4]Division of Engineering and Applied Science, California Institute of Technology; [5]Department of Physics, University of Houston; [6]Department of Electrical Engineering and Computer Science, MIT

As the critical dimensions of a wide range of emerging technologies, from consumer electronics to nanoscale energy conversion systems, get ever smaller, the importance of having a fundamental understanding of the material properties gets ever larger. The behaviors of electrons and photons, electronic and electromagnetic energy carriers respectively, have been widely studied both experimentally and theoretically. By exploiting their wavelike characteristics, the transport properties of these energy carriers can now be tailored using artificial nanostructures. By comparison, a fundamental understanding of the behavior of phonons, a major thermal energy carrier, in the presence of material interfaces, boundaries, or defects has remained elusive, hampering the ability to tailor the thermal properties of materials and nanostructures. This work aims at enhancing the understanding of the fundamental properties of phonons by examining their wavelike nature, or coherence, during thermal conduction. Coherent phonons maintain wavelike characteristics and experience predictable interference effects whereas incoherent phonons are expected to lose phase information at materials boundaries and interface.

Since thermal transport involves broadband phonons, the challenge lies in discerning the coherent and incoherent contributions to heat conduction. To address this challenge, superlattices (SLs) comprised of periodic layers of GaAs and AlAs thin films on the order of 10 nm in thickness, were synthesized (Fig. 1A). In contrast with most SL-based studies of phonon behavior, the thicknesses of the individual layers were held constant while the total number of periods was varied. This approach gives unique access to the changing role of coherent phonons during heat conduction. The temperature-dependent thermal conductivities of the SLs were measured using the time-domain thermoreflectance technique and were shown to increase nearly linearly with total sample thickness (Fig. 1B), indicating the presence of coherent phonon heat conduction. The results of this experimental study, in tandem with computational results from both density functional theory (DFT, Fig. 1C) and Green's function calculations showed for the first time the important role of coherent phonons during thermal transport.

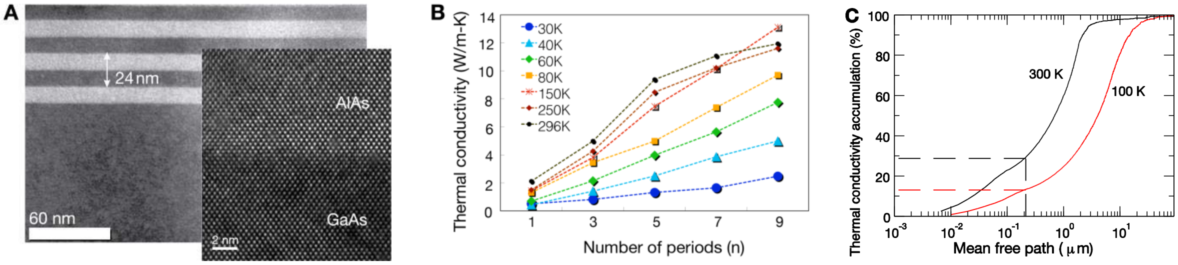


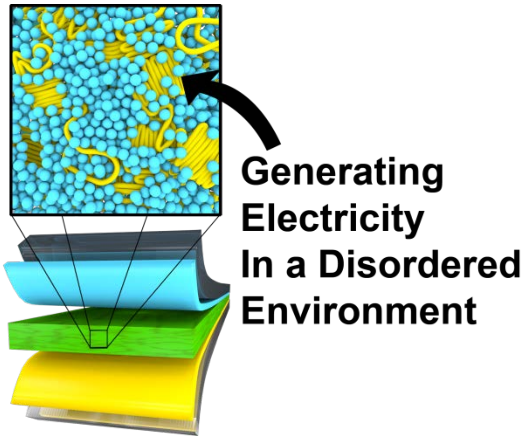
Figure 1 (A) TEM and HRTEM images of GaAs/AlAs SL; (B) Time-domain thermoreflectance measurements show increasing thermal conductivity with increasing number of periods; (C) first-principles calculations of the SL thermal conductivity accumulation functions show the importance of coherent phonons and agree well with experimental results.

M.N. Luckyanova, J. Garg, K. Esfarjani, A. Jandl, M.T. Bulsara, A.J. Schmidt, A.J. Minnich, S. Chen, M.S. Dresselhaus, Z. Ren, E.A. Fitzgerald, and G. Chen. *Science* **338**, 936-9 (2012).

CONCERTED PROCESSES IN ORGANIC PHOTOVOLTAICS: THE RELATED CHALLENGES OF GENERATING AND COLLECTING CHARGE IN A DISORDER ENVIRONMENT.

[ANSER] Brett M. Savoie[1]; Henry Heitzer[1]; Brian S. Rolczynszki[1]; Bijan Movaghar[1]; Stephen Loser[1]; Sylvia Lou[1]; Luping Yu[1,2]; Lin X. Chen[1,3]; Tobin J. Marks[1]; Mark A. Ratner[1]

[1]Northwestern University; [2]University of Chicago; [3]Argonne National Laboratory



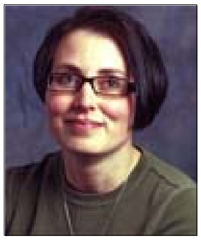
Remarkable progress has been made towards increasing the efficiencies of organic photovoltaic cells (OPVs) in the past few years, with cells based on solution-processed blends of conjugated polymers and fullerenes routinely showing near unity quantum efficiencies. However, the question of how such high efficiencies can be achieved in disordered materials with low dielectric constants remains unanswered. Existing models based on the Marcus and Onsager frameworks fail to explain many of the experimental results on charge generation, lack predictive power, and offer no insight into the origin of the fullerene's success as an electron acceptor in these systems.

Using a joint theoretical and experimental approach, uniquely achievable through the ANSER Center and involving four center principal investigators, I show that the crucial ingredient for efficient charge generation is the participation of many molecules in the process. Using ultrafast optoelectronic experiments and large-scale many-molecule modeling, we find that aggregates of organic semiconductors, like fullerenes, can sustain delocalized states over several molecules. Critically, these states are robust to disorder, owing to the unique spherical topology of the fullerene component and its degenerate unoccupied electronic levels. Proceeding from this discovery we find that several experimentally observed, but unexplained, features of charge generation can be understood by moving away from single molecule descriptions and considering the emergent properties of ordered arrays of molecules.

These insights into charge generation are complemented by recent work on charge collection from the ANSER Center. Unity quantum efficiencies also imply perfect collection efficiency of the generated charge. However, under operating conditions and away from short circuit, we often observe that collection efficiency drops, resulting in low FF. From recent modeling work and an examination of small molecule systems developed within ANSER, I trace the connection between increased disorder and why many optimized device thicknesses are less than the absorption length of the active materials.

Emphasis is placed throughout on the discovered overlaps between challenges facing both problems, the means for overcoming disorder, and the unique opportunities the collaborations fostered by the ANSER Center have provided.

POSTDOCTORAL RESEARCHER WINNERS



PROBING LIGHT HARVESTING AND PHOTOSYNTHETIC PRODUCTIVITY IN CYANOBACTERIA

[PARC] Michelle Liberton[1], Lawrence Page[1*], Aaron M. Collins[2], William B. O'Dell[3], Hugh O'Neill[3], Volker S. Urban[3], Jerilyn A. Timlin[2], and Himadri B. Pakrasi[1]
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Photosynthetic antenna systems function in the process of converting sunlight into cellular fuel, a topic of considerable interest in bioenergy research. In the cyanobacterium *Synechocystis* sp. PCC 6803, light harvesting is accomplished by a combination of membrane intrinsic pigment-proteins and large extrinsic phycobilisome complexes. The phycobilisomes associate with the cytoplasmic surface of thylakoid membranes, and studies have shown that modulation of phycobilisome size results in changes to the membrane spacing (1). We have used a combination of approaches to explore the consequences of antenna modification in terms of physiology and membrane morphology and dynamics in wild-type *Synechocystis* 6803 and a series of mutants with varying degrees of phycobilisome truncation. Our work using transmission electron microscopy (TEM), hyperspectral confocal fluorescence microscopy (HCFM), small angle neutron scattering (SANS), and an optimized photobioreactor system have revealed the adaptive strategies that cells employ to compensate for antenna reduction. As the phycobilisome antenna was truncated, large-scale changes in thylakoid morphology were observed, accompanied by increased physical segregation of the two photosystems (2). Repeating distances between thylakoid membranes measured by SANS were correlated with TEM data, and corresponded to the degree of phycobilisome truncation (3). We found that cyanobacterial membranes have a high degree of structural flexibility, and that changes in the membrane system upon illumination are rapid and reversible (3). Phycobilisome truncation in *Synechocystis* 6803 did not confer an advantage in growth or biomass accumulation, in contrast to predictions from algal models (4). These results highlight the dynamic nature of the intracellular membrane system in cyanobacterial cells and suggest an adaptive strategy that allows cells to compensate for decreased light harvesting capability.

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(2) Collins AM, Liberton M, Jones HD, Garcia OF, Pakrasi HB, Timlin JA. (2012) Plant Physiol 158: 1600-09.
(3) Liberton M, Page LE, O'Dell WB, O'Neill H, Urban VS, Pakrasi HB. (2013) J Biol Chem 288: 3632-40.
(4) Page LE, Liberton M, Pakrasi HB. (2012) Appl Environ Microbiol: 78: 6349-51.

This material is based upon work supported as part of the Photosynthetic Antenna Research Center (PARC), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC 0001035. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. The Bio-SANS instrument is a resource of the Center for Structural Molecular Biology at Oak Ridge National Laboratory that is supported by the U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research Project ERKP291. Bio-SANS is located at the Oak Ridge National Laboratory's High Flux Isotope Reactor. The neutron source is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

ADSORBATE INDUCED ADATOM MOBILITY IN A MODEL CATALYST: PD/FE$_3$O$_4$

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Industrial catalysts often comprise metal nanoparticles residing on a metal-oxide support. As part of the center for atomic level catalyst design, we are searching for model systems that will allow us to disentangle the fundamental processes underlying heterogeneous catalysis, and with which to test the limits of current theoretical modeling. Recently, we discovered that the Fe_3O_4(001) surface[1] stabilizes single metal adatoms of catalytically active metals to high temperatures; Au atoms, for example, remain isolated up to 400 °C[2]. This remarkable property facilitates very interesting, previously impossible, experiments. For example, one can test the hypothesis of "single-atom catalysis" to unambiguously show whether single atoms can really catalyze chemical reactions. If single atoms are catalytically active, the amount of precious metal required, and with it much of the cost of a catalyst, could be slashed.

In this presentation, we use the Fe_3O_4(001) adatom template to investigate how gas molecules affect the stability of a model Pd/Fe_3O_4 catalyst[3]. Under ultrahigh vacuum conditions, atomically resolved scanning tunneling microscopy (STM) movies show that single Pd atoms are completely stationary over many hours. In the presence of CO, however, highly mobile Pd-carbonyl species form, and mass transport is initiated at the surface. When a critical number of Pd-carbonyls meet, clusters nucleate. The cluster nuclei are themselves mobile, diffusing across the surface, collecting nearby adatoms until a stable size is reached. Tracking the evolution of the system atom-by-atom allows all the details of the sintering process to be discerned. Complementary DFT calculations show that CO lifts the Pd atoms from the surface, vastly reducing the barrier for diffusion One particularly interesting finding is that reaction with surface hydroxyl groups stabilizes Pd atoms against carbonyl formation, preventing the sintering mechanism. These results shed new light on the sintering process, and hint that pretreatment with relevant molecules could be a viable strategy for extending catalyst lifetimes.

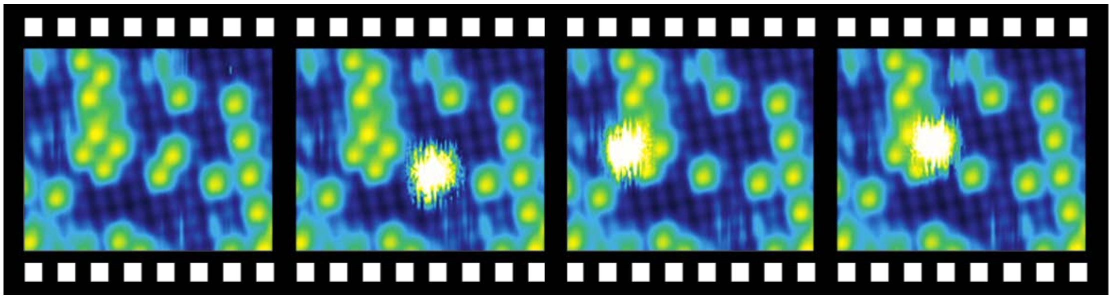

Figure 1: Selected frames from an STM movie showing the formation and subsequent mobility of a Pd-carbonyl in the Pd/Fe_3O_4(001) model catalyst

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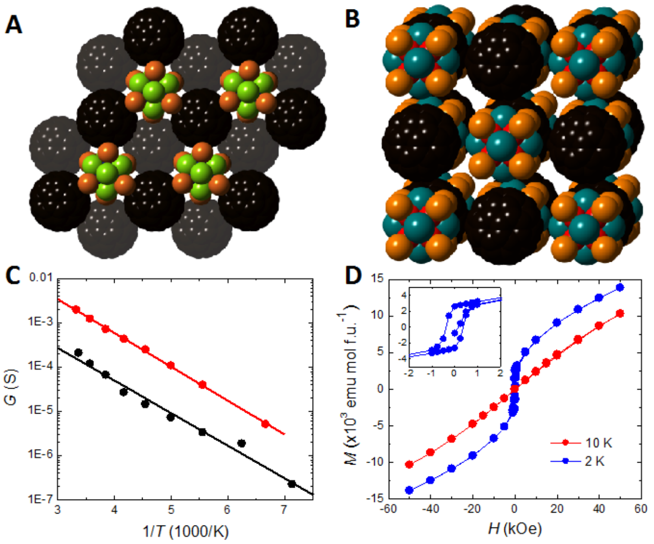
2. Z. Novotny, G. Argentero, Z. Wang, M. Schmid, U. Diebold, G.S. Parkinson, Phys. Rev. Lett., 108, 216103 (2012)
3. G. S. Parkinson Z. Novotny, G. Argentero, M. Schmid, J. Pavelec, R. Kosak, P. Blaha, U. Diebold, Nature Materials, in press (2013).

NANOSCALE ATOMS IN SOLID-STATE CHEMISTRY

[RPEMSC] Xavier Roy[1], Chul-Ho Lee[1,2], Andrew C. Crowther[3], Christine L. Schenck[1], Tiglet Besara[4], Roger A. Lalancette[6], Theo Siegrist[4,5], Peter W. Stephens[7], Louis E. Brus[1], Philip Kim[2], Michael L. Steigerwald[1], Colin Nuckolls[1]
[1]Department of Chemistry, Columbia University, New York, NY 10027 (USA) *http://nuckolls.chem.columbia.edu/*; *[2]Department of Physics, Columbia University, New York, NY 10027 (USA); [3]Department of Chemistry,* Barnard *College, New York, NY 10027 (USA); [4]National High Magnetic Field Laboratory, FSU, Tallahassee, FL 32310 (USA); [5]Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, FL 32310 (USA); [6]Department of Chemistry, Rutgers State University, Newark, NJ 07102 (USA); [7]Department of Physics and Astronomy, SUNY Stony Brook, Stony Brook, NY 11794 (USA)*

Conventional binary solid-state compounds, A_xB_y, are infinite, crystalline arrays of atoms A and B. In this work, we describe analogous binary solids in which the 'atomic' building blocks are pseudo-spherical molecular clusters rather than simply atoms. We combine independently prepared electronically and structurally complementary molecular cluster building blocks to form atomically precise binary solid-state compounds. When the building blocks are atoms (ions), binary solids assemble into simple crystalline arrays such as the rock-salt and CdI_2 lattices. We show that when similarly-sized clusters combine the same lattice results, albeit at the dramatically increased length scale of nanometers rather than Angstroms. The internal structures of the constituent clusters remain unchanged, but charge is transferred between them, forming ionic solids analogous to NaCl. We show that we can tune the structural, electronic, and magnetic properties of our artificial atoms and assemble crystalline solids that exhibit collective physical properties. In these materials, the constituent clusters are able to interact electronically and the assemblies show activated electrical transport with activation energies of 100 to 150 meV and spontaneous magnetic ordering at low temperature, akin to atoms in a solid-state compound. These results chart a clear path to creating whole families of multi-functional solid-state materials whose electronic and magnetic properties can be tuned by varying the constitution of the superatom building blocks.



Space filling molecular structure of (A) $Co_6Se_8(PEt_3)_6{\bullet}2C_{60}$ showing the crystal packing looking down the *ab* plane and of (B) $Ni_9Te_6(PEt_3)_8{\bullet}C_{60}$. Carbon, black; nickel, red; cobalt, blue; phosphorus, orange; tellurium, teal; selenium, green. The ethyl groups on the phosphines were removed to clarify the view. (C) Plot of the conductance (*G*) vs. 1/*T* for $Co_6Se_8(PEt_3)_6{\bullet}2C_{60}$. The four probes conductance measurements were done on a single crystal (black) and a pressed pellet (red). The Arrhenius fits are shown as solid lines. (D) Magnetization (*M*) as a function of applied field (*H*) at 10 K and 2 K for $Ni_9Te_6(PEt_3)_8{\bullet}C_{60}$. The inset shows the enlarged magnetic hysteresis at 2 K.

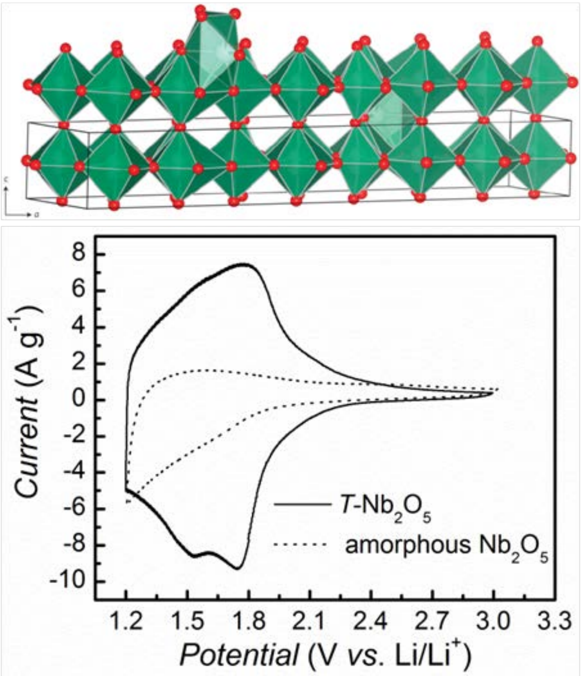
GRADUATE STUDENT FINALISTS

High-rate electrochemical energy storage with Nb_2O_5

[MEEM] Veronica Augustyn[1], Jeremy Come[2], Michael A. Lowe[3], Jong Wuong Kim[1], Pierre-Louis Taberna[2], Sarah H. Tolbert[4], Hector D. Abruña[3], Patrice Simon[2], and Bruce Dunn[1]

[1]Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, USA; [2]Department of Materials Science, Université Paul Sabatier, CIRIMAT UMR CNRS 5085, Toulouse 31062, France; [3]Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, USA; [4]Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, USA

The need for more abundant, clean, efficient, and secure energy is opening up applications for electrochemical energy storage (EES) beyond portable electronics. While the opportunities for EES are very promising, these devices still suffer in performance due to material limitations. One challenge for EES is to design electrode materials that can provide high power and high energy densities simultaneously. The research presented here will examine how such electrode materials are possible through the use of pseudocapacitive energy storage. Pseudocapacitance was first noted in 1971 in hydrous RuO_2; research over the past several decades has focused on identifying materials that exhibit the same properties as RuO_2 but at a lower cost. In hydrous RuO_2, protons from the electrolyte adsorb onto the inner and outer surface areas of the material. Here, a different pseudocapacitive mechanism is identified in orthorhombic *T*-Nb_2O_5, termed intercalation pseudocapacitance. This mechanism leads to the same type of rapid kinetic behavior expected for capacitive charge storage but it occurs due to the intercalation of Li^+ into the bulk of *T*-Nb_2O_5. For charging times up to 60 seconds, no diffusion limitations are observed and this is what results in the high-rate capability of the material. The intercalation pseudocapacitance mechanism is beneficial for device applications because it does not require materials with ultrahigh surface areas that need to be exposed to the electrolyte. In addition, a set of analytical tools is presented for the facile identification of such rapid energy storage reactions and these can be applied to other materials of interest. This work has been recently published in *Nature Materials (V. Augustyn et. Al., "High Rate Electrochemical Energy Storage via Li+ Intercalation Pseudocapacitance" Nature Materials, 12, 518-522 (2013)* [DOI: 10.1038/NMAT3601]).



Top: Crystal structure of *T*-Nb_2O_5 stacked along the *c* axis demonstrates the layered arrangement of oxygen (red) and niobium (within polyhedra) atoms along the *a-b* plane. This structure accounts for the rapid Li^+ charge storage kinetics in this material. **Bottom**: Cyclic voltammetry at 10 mV s^{-1} of amorphous and *T*-Nb_2O_5 in a non-aqueous Li^+ electrolyte. While the surface area of the amorphous material is more than 2X higher than that of the crystalline material, the *T*-Nb_2O_5 exhibits both higher and faster charge storage. This result indicates that charge storage is not limited to the surface in Nb_2O_5.

SOLID, POROUS MATERIAL FOR IMPROVED EFFICIENCY OF GASOLINE PRODUCTION AND LOW-COST AND NON-TOXIC ENHANCEMENT OF GASOLINE QUALITY

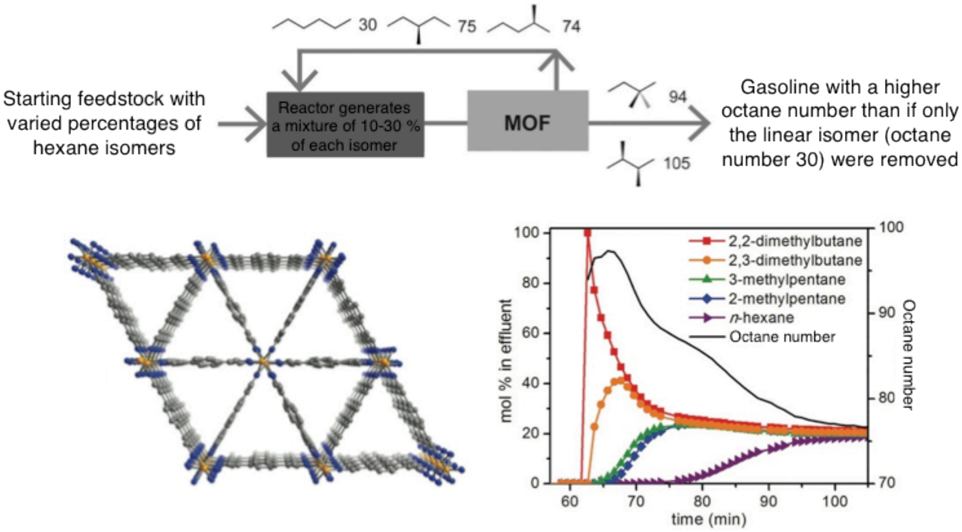
[CGS] Zoey R. Herm,[1] Brian M. Wiers,[1] Jarad A. Mason,[1] Jasper M. van Baten,[2] Norberto Masciocchi,[3] Rajamani Krishna,[2] Jeffrey R. Long[1]

[1]Department of Chemistry, University of California, Berkeley, CA 94720, USA. [2]Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, Netherlands.. [3]Dipartimento di Scienza e Alta Tecnologia, Università dell'Insubria, via Valleggio 11, I-22100 Como, Italy.

The discovery presented here could render the refining of petroleum more efficient and, as a result, save substantial energy worldwide. Further, if fewer low octane number hydrocarbons were added to gasoline, fewer toxic additives would be required to boost quality – benefiting both human health and the environment.

Saturated hydrocarbons such as pentane (C_5H_{12}), hexane (C_6H_{14}), and heptane (C_7H_{16}) each have multiple isomers in which the same number of carbons can be connected linearly or with branch points. These isomers are components of gasoline and have drastically varying value in the petroleum industry due to their wide-ranging octane numbers. Currently, some of the low-quality isomers end up in gasoline because they cannot be removed efficiently, and high-octane additives which require energy to generate and also are often toxic are added to the gasoline to compensate.

Through collaboration between theoretical modeling and the development of new experimental techniques (bottom right below), the solid iron based material $Fe_2(BDP)_3$ reported here (bottom left below) was pinpointed and shown to efficiently separate the most valuable isomers because of the rare triangular shape of its pores.



Top: Schematic of the proposed hexane isomer separation. The numbers next to the hexane isomers are octane numbers. *Bottom Right:* The crystal structure of $Fe_2(BDP)_3$ showing Fe (orange), N(blue), and C(gray) atoms, viewing along the *c*-axis. *Bottom Left:* Results of a breakthrough experiment in which a mixture of hexane isomers were moved through a bed of $Fe_2(BDP)_3$. The more valuable dimethylbutane isomers elute first and are therefore possible to separate.

Herm, Z. R.; Wiers, B, M.; Mason, J. A.; van Baten, J. M.; Hudson, M. R.; Zajdel, P.; Brown, C. M.; Masciocchi, N.; Krishna, R.; Long, J. R. *Science* **2013**, *340*, 960-964.

REACTION DYNAMICS OF A NANOMETER-SIZED URANYL CLUSTER IN SOLUTION

[MSA] Rene L. Johnson;[1] C. André Ohlin;[2] Kristi L. Pellegrini;[3] Peter. C. Burns;[3,4] William H. Casey[1,5]

1.Department of Chemistry, University of California - Davis, Davis, CA (USA); 2. School of Chemistry, Monash University, Clayton, Victoria (Australia); 3. Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, South Bend, IN (USA); 4. Department of Chemistry and Biochemistry, University of Notre Dame, South Bend, IN (USA); 5. Department of Geology, University of California – Davis, Davis, CA (USA)

A large and previously unsuspected class of uranyl-peroxide clusters was discovered less than a decade ago as nanometer-size ions that form spontaneously in aqueous solutions. Little is known about the chemistry of these ions in spite of their obvious importance as soluble forms of actinide elements which are potentially present in the environment. Here we show reversible structural changes in an example uranyl(VI) cluster of this class that is ~2 nm in diameter. It contains 24 uranyl moieties, and 12 pyrophosphate units that are detectable via ^{31}P NMR and has a nominal stoichiometry of $[(UO_2)_{24}(O_2)_{24}(HP_2O_7)_6(H_2P_2O_7)_6]^{30-}$. NMR spectroscopy shows that the ion has two distinct forms, aspherical and spherical, that interconvert (Figure 1. Left) on the millisecond to second time scale depending upon temperature and the size of the counterions. For a solution with only Na^+ counterions we estimated $k_{298} = 9.7\pm0.6\ s^{-1}$, as compared to $k_{298} = 0.40\pm0.02\ s^{-1}$ estimated for a solution with Na^+ and tetramethyl ammonium counterions. This dynamic interconversion (Figure 1. Right) may relate to the onset of dissociation of the cluster into smaller fragments. High-pressure (up to 300 MPs) experiments yielded an activation volume of $\Delta V^{\ddagger} = +11.6\pm0.5\ cm^3\ mol^{-1}$, showing that the difference in volume between the isomers is about the volume of a water molecule. Extrapolated broadly, these results support a model where nanometer-size features at the oxide-solution interface have sets of accessible low-energy metastable states that control isotope exchanges and dissociation.

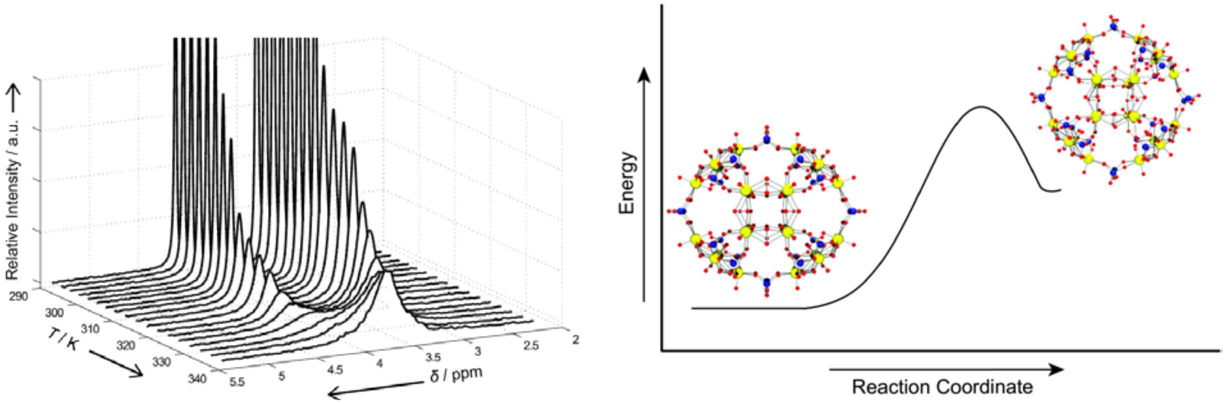


Figure 1. **Left:** Stacked ^{31}P solution-NMR plot of the uranyl-peroxo-pyrophosphate cluster as a function of temperature. This plot shows the interconversion of the aspherical form of the cluster to the spherical form. **Right:** A proposed reaction coordinate for the conformational change from the stable aspherical molecule to the metastable spherical molecule.

* R. L. Johnson, C. A. Ohlin, K. Pellegrini, P. C. Burns, W. H. Casey, *Angew. Chem. Int. Ed.* **2013**, In Print. DOI: 10.1002/anie.201301973

NANO-ENGINEERING OF SILICON NANOSTRUCTURES FOR LITHIUM-ION BATTERIES AND ENERGY STORAGE DEVICES

[NEES] Khim Karki[1], Chuanfu Sun[2], Eric Epstein[1], Jeong-Hyun Cho[3], Zheng Jia[4], Yujie Zhu[5] Teng Li[4], Yue Qi[6], Tom Picraux[3], Gary Rubloff[1], Chunsheng Wang[5], YuHuang Wang[2], and John Cumings[1]

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The rising demand of energy consumption with virtually depleted natural fuel resources requires the utilization of alternative sources such as solar and wind power. However, the intermittent nature of energy generated from these resources would be unable to meet the threshold of the on and off peak energy demands. Thus, high-performance electrical energy storage technology is desirable to enable clean, efficient and uninterruptible power supply to the consumer. Lithium-ion batteries, among many other storage technologies can store significantly more energy per unit mass (energy density), naturally becoming the best contender to manage renewable resources and achieve economic sustainability.

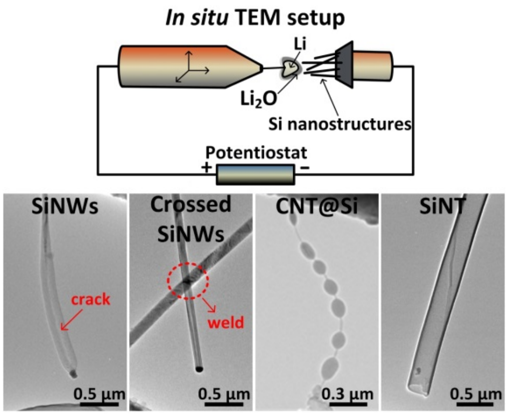

Fig.1: *In situ* TEM setup and silicon nanostructures studied

Recently, it has been proposed that silicon-based nanostructures could be used as lithium storage materials with greatly enhanced storage capacities over that for conventional graphite anodes in the next generation of lithium-ion batteries. However, the studies to date have shown that the nanomaterials, while better, are still not good enough to withstand a large number of lithiation cycles, and moreover, there is insufficient fundamental insight into the science of the improvements or the advances necessary before widespread adoption. Therefore, we conduct real-time investigations of individual silicon nanostructures by fabricating prototype nanoscale electrochemical cells inside a transmission electron microscope (TEM). Using this pioneering technique, we have studied the structural, electrochemical, and mechanical properties of several one-dimensional nanostructures such as silicon nanowires (SiNWs), carbon nanotube@silicon (CNT@Si) heterostructures, and silicon nanotubes (SiNTs) as shown in Fig. 1. While cracking and pulverization are known to be mitigated in part by nanostructured forms of silicon, such as nanowires, several recent studies indicate that cracking can still occur in nanostructures under a variety of conditions. We also observe an opposite effect in which physically distinct SiNWs can become fused through an electrochemically-induced process, which suggests that this welding may lead to self-healing in nanostructured Si-electrodes. Our results show evidence of robust weld strength and facile transport of lithium ions across the welded Si-Si interface, both desirable properties for enhanced battery performance. Similarly, CNT@Si beaded-string heterostructures with chemically tailored carbon–silicon interfaces were designed and synthesized based on a fundamental understanding of carbon surface chemistry and Si nucleation on covalently modified CNT surfaces. *In situ* TEM studies of lithiation propagation reveal that these novel heterostructures can accommodate massive volume changes during lithiation and delithiation without appreciable mechanical failure. These findings thus provide important new insights in the design of high performance Si electrodes, laying a foundation for next-generation lithium ion batteries.

This work was initiated and supported as part of Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy.

UNDERSTANDING CRYSTALLINE CELLULOSE MICROFIBRILS ASSEMBLY IN PLANT CELL WALLS USING SUM-FREQUENCY-GENERATION (SFG) VIBRATION SPECTROSCOPY

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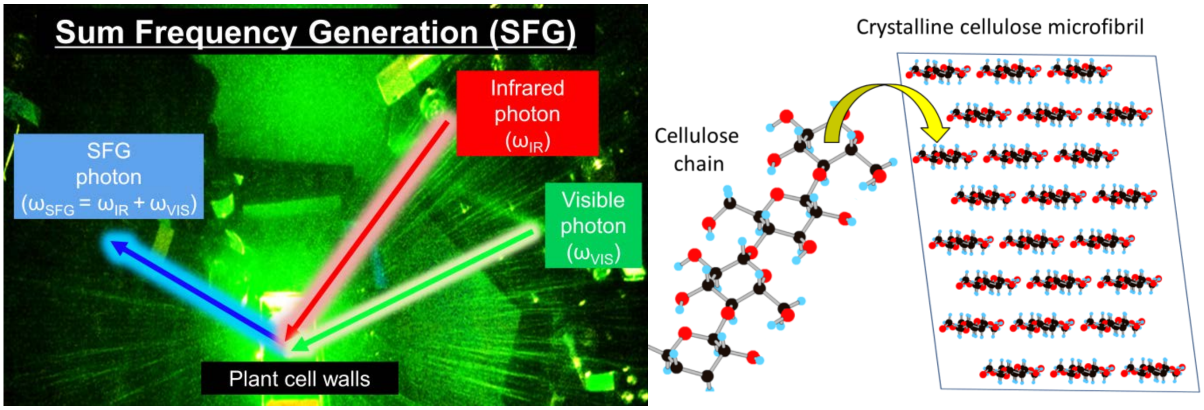
Plant cell walls constitute the most abundant biomass usable for production of chemicals and transportation fuels, but they are highly recalcitrant to biochemical transformation processes. This is in part due to the crystalline nature of cellulose and its interactions with other matrix polymers in cell walls. The organization or assembly of crystalline cellulose with matrix polymers also varies depending on developmental stages of the plant as well as plant species. Thus, understanding the crystalline structure and hierarchical organization of cellulose in plant cell walls could greatly advance science-based efforts to economical transportation fuels from biorenewable sources. We use sum-frequency-generation (SFG) vibration spectroscopy to probe crystalline cellulose in intact cell walls and provide the structural information of cellulose microfibril arrangements over a length scale of 100s of nm. In this talk, we show the changes in cellulose ordering in intact young (primary) and mature (secondary) plant cell walls from *A. thaliana* and *G. hirsutum* (cotton). The SFG analysis of these plant samples revealed that crystalline cellulose microfibrils are organized differently in plant cell walls at different growth stages. When the samples were treated by standard methods of purify cellulose from plant cell walls, which has been the main approach for structural analysis of cellulose in biomass, cellulose organization in the wall was disturbed. Thus, SFG offers unprecedented opportunity to reveal important organizational features of cellulose within cell walls at different developmental stages and in lignocellulosic biomass harvested from different sources and pretreated for more efficient biochemical conversion to sugars and other chemicals.



Images: SFG signals generated by plant cell walls is based upon spectral addition (left) occurring in ordered arrangements of crystalline cellulose microfibrils (right).

ELECTROCATALYSIS OF TOTAL WATER SPLITTING ON PEROVSKITE OXIDES AND OXYNITRIDES

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Perovskite oxides and oxynitrides have recently been the subject of multiple screening studies to determine which materials have bandstructures conducive to overall water splitting [1,2]. However, such screening studies neglect the effect of kinetic overpotentials for oxygen evolution (OER) and hydrogen evolution (HER). In the present work, we use density functional theory (DFT) calculations to describe the limiting potentials for both OER and HER on various perovskite materials. From our results, we derive scaling relations for the binding energies of H_2O oxidation intermediates that are compatible with well-established theoretical descriptions of oxide materials for OER [3]. Using this approach, we comment on the stability and surface structure of perovskites in the electrochemical environment. Most importantly, we demonstrate that perovskite photoelectrocatalysts with bandgaps suitable for total water splitting may have kinetic limitations that make co-catalysts necessary, as shown in Figure 1. We also determine the theoretical overpotentials of a larger dataset of perovskite compounds for both OER and HER in order to identify trends in activity for these electrodes in water splitting devices.

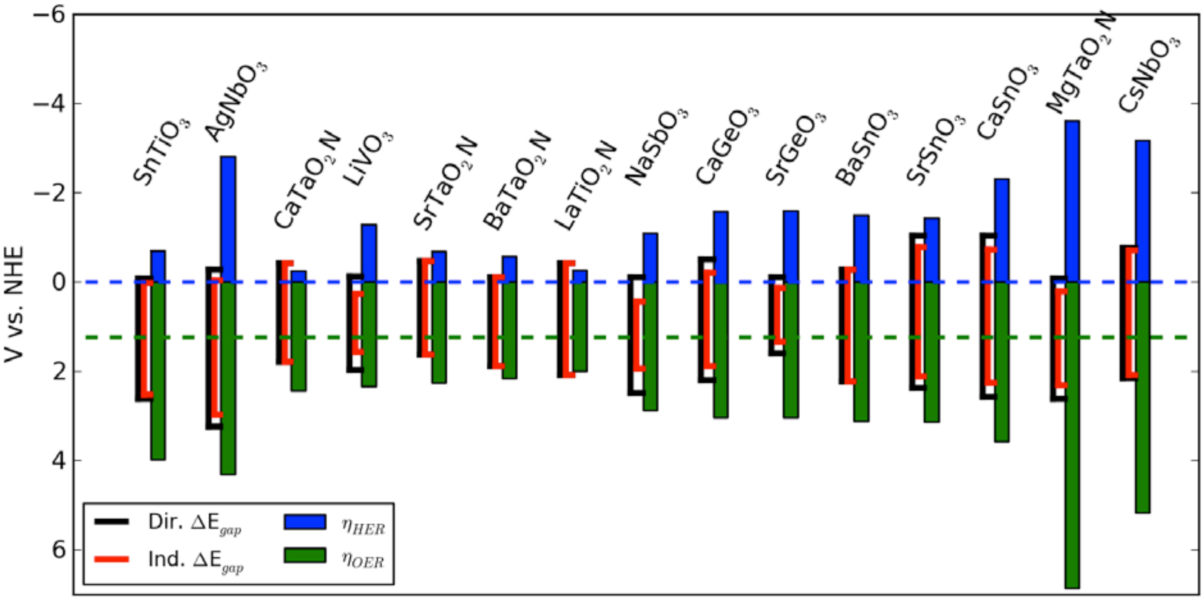

Figure 1 - Theoretical overpotentials and bandgaps for HER and OER on screened materials [1]

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STABILIZATION BY ATOMIC LAYER DEPOSITION OF COPPER CATALYSTS FOR LIQUID PHASE REACTIONS

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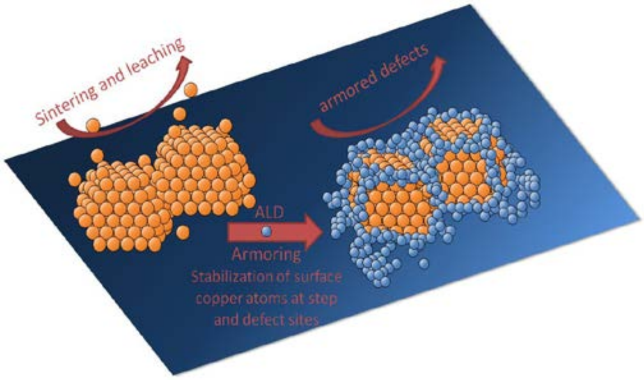

Precious metal catalysts are used extensively in the petrochemical industry and are anticipated to have a significant role in future biorefineries. While it would be desirable to replace precious metal catalysts (e.g., platinum) with base metals that are more abundant (e.g., copper), these base metal catalysts are susceptible to sintering and leaching under liquid-phase reaction conditions. Atomic layer deposition (ALD) of an alumina coating can be employed to stabilize a base-metal catalyst (e.g., copper) for liquid-phase catalytic reactions (e.g., hydrogenation of biomass-derived furfural in alcohol or water solvents), thereby eliminating the deactivation of conventional catalysts by sintering and leaching into the reaction medium. This method of catalyst stabilization reduces the need to employ precious metals (e.g., platinum) in liquid-phase catalytic processing. The alumina overcoat initially covers the active catalyst surface completely. We show using solid state nuclear magnetic resonance, powder X-ray diffraction, and electron microscopy that high temperature treatment (973 K) opens porosity in the overcoat by forming crystallites of γ-Al_2O_3. Infrared spectroscopic measurements, density functional theory, and scanning tunneling microscopy studies of trimethylaluminum ALD on Cu(111) show that the remarkable stability imparted to copper nanoparticles arises from selective armoring of highly under-coordinated copper atoms on the nanoparticle surface by the overcoating alumina.

The ability to stabilize base metals could have important applications beyond catalysis such as in electronics and especially in batteries. This project is an example of how IACT's collaborative structure brings together advanced synthesis, experimentation, theory, and characterization to advance fundamental scientific understanding and provide breakthrough solutions to real world problems.

HYPERVALENT SURFACE INTERACTIONS FOR COLLOIDAL STABILITY AND DOPING OF SILICON NANOCRYSTALS

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Solar cells based on colloidal nanocrystals (NCs) are a prominent example of so-called third-generation of photovoltaics (PVs), which seek high efficiencies from low cost devices through exploitation of advanced physical phenomena. NCs can be inexpensively processed from solution in the same way numbers are screen-printed onto little league baseball jerseys. At the same time, they offer the unique ability to capture the excess energy of solar photons that is lost as heat in conventional PV devices by creating extra current through a process known as multiple exciton generation (MEG).

MEG is now routinely measured in NCs isolated in solution; however, multiple excitons are only useful for harnessing solar energy if they can be efficiently extracted when assembled into a PV device. There are two significant barriers to achieving this. The first is coping with the insulating ligands on the NC surfaces that provide the colloidal stability needed to deposit thin film devices. Secondly, the use of intentional impurities, or dopants, is paramount to achieving conductive films and internal electric fields needed for efficient charge carrier extraction. Recently, we demonstrated a new surface chemistry technique that confronts both of these challenges *simultaneously*.[1] Silicon NCs featuring chlorine termination exhibit a unique surface polarization that renders surface silicon atoms electron deficient, and therefore Lewis acidic and susceptible to hypervalent interactions with donor molecules. These donor molecules not only stabilize NCs into colloidal solution *without ligands*, but also produce controllable *n*-type doping in the NCs that can be retained in deposited films.

We believe this study on silicon NCs is a proof-of-concept of a more general approach to providing colloidal stability, facile thin film deposition, and doping of NCs. Thus, it may represent only the first of many efforts to explore the application of hypervalent interactions between a range of NC materials and surface dopants for improved performance in NC-based PV devices.

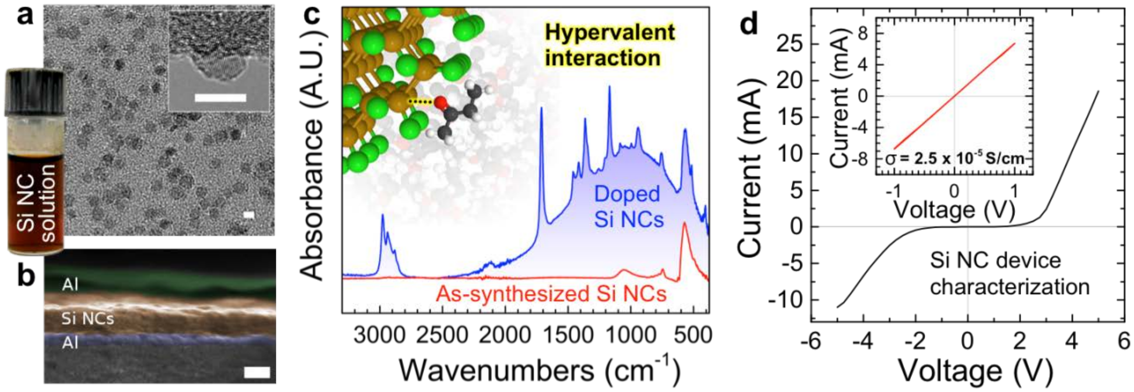

Figure 2: Cl-terminated Si NCs form a stable colloidal solution Lewis basic solvents. Si NCs are solvated without bound ligands, which can be seen the transmission electron micrograph (a) (scale is 8 nm). Films of Si NCs can be cast from the solution to fabricate optoelectronic devices (b) (scale is 2 µm). Colloidal stability is derived from hypervalent interactions at the Si NC surface. The interaction also provides doping, observed as a free carrier absorption using infrared spectroscopy (c, blue spectrum). Preliminary experiments suggest these carriers are active in optoelectronic devices (d).

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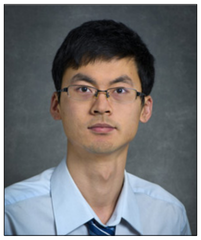

CONTROLS ON MINERALIZATION IN VOLCANOGENIC RESERVOIR ROCKS

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We proposed to use volcanogenic sandstones for CO_2 sequestration. Such sandstones with a relatively high percentage of volcanic rock fragments (VRF) could be a promising target for CO_2 sequestration in that they have a sufficient percentage of reactive minerals to allow substantial mineralization of injected $scCO_2$, which provides the most secure form of CO2 storage, but can also be porous and permeable enough to allow injection at acceptable rates. The limitation in using volcanogenic sandstones as CO_2 reservoir rocks is that porosity and permeability tend to decrease with increase of volcanic rock fragments (VRF) and with the length and complexity of the diagenetic history. Decreased porosity limits the rate at which CO_2 can be injected. We evaluated these tradeoffs to assess the feasibility of using volcanogenic sandstone to achieve highly secure CO_2 storage. Using relationships between VRF percent, porosity and permeability from available geological data, the reactive transport code TOUGHREACT was used to estimate the rate and extent of CO_2 mineralization over 1000 years, and the trade-off between higher reactivity and lower porosity and permeability. For the parameter set that we believe is defensible, the optimal VRF percent for the largest amount of mineralized CO_2 is around 10-20%. The results show that as much as 80% CO_2 mineralization could occur in 1000 years and still allow sufficient injectivity so that ca. 1 megaton of CO_2 can be injected per year per well. The key to estimating how much CO_2 can be injected and mineralized is the relationship between permeability (or injectivity) and reactive mineral content. The overall relationships can be reduced to a simple equation that relates the fraction of injected CO_2 that becomes mineralized in 1000 years to the volume fraction of reactive minerals. We have sampled examples of volcanogenic sandstones from Miocene Etchegoin Formation, central California to examine these relationships. Characterizations of these samples by SEM, XRF and XRD show that they are very rich in reactive minerals with around 32% plagioclase, 10% clinopyroxene, 2% diopside, and 1% ilmenite. Porosities range from 10% to 20%, and permeabilities range from 10 mD to 1000 mD. Batch experiments are also in progress to obtain realistic reactivity estimates.

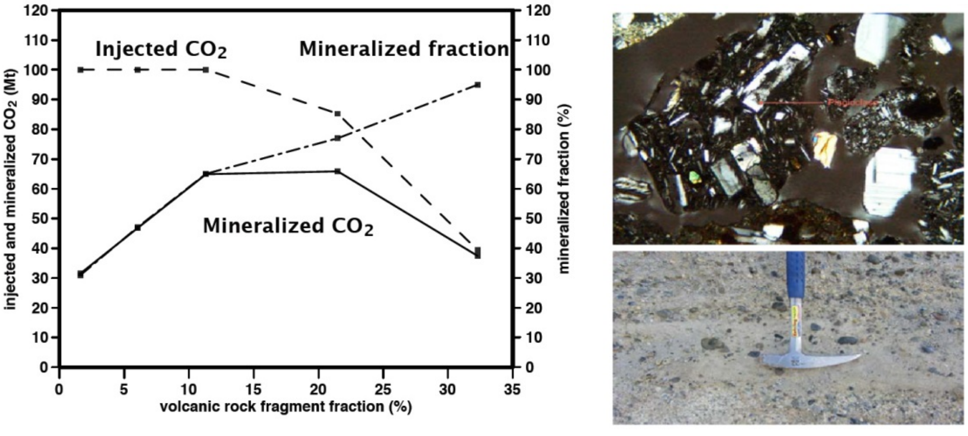
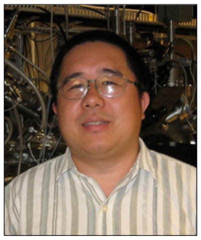


Figure 1. (Left) Amount of injected CO_2, mineralized CO_2 and mineralized fraction for different volcanic rock fragment (VRF) fractions, showing the largest amount of mineralized CO_2 at around VRF =10%-20%. (Right) Photomicrograph and outcrop photo showing volcanic mineralogy and abundant pore space from Miocene Etchegoin Formation, central California



GROWTH OF NOVEL SUPERCONDUCTORS BY ATOMIC LAYER BY LAYER MOLECULAR BEAM EPITAXY

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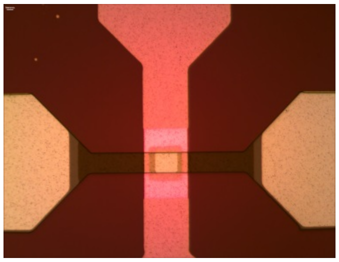
We have studied the growth of novel superconducting phases and multilayers involving them using Atomic Layer by Layer Molecular Beam Epitaxy (ALL-MBE). This growth technique is accurate enough to sequence the atomic layer content of crystalline samples so as to form new phases, heterojunctions with clean and flat interfaces as well as device structures for investigating fundamental properties of high Tc superconductors.

In one set of experiments we investigated the growth and physical properties of films and superlattices of LnT_2Ge_2, where Ln was La or Ce and T was Fe or Cu. The Ce compounds were heavy fermions and the Ce magnetism was found to be strongly coupled to the itinerant states below around 20 K. Since $CeCu_2Ge_2$ is superconducting, this may allow us to investigate spin mediated electron pairing in a system other than cuprates.

We have also studied how oxygen dopes FeTe films to make them superconducting. We found that oxygen can interact with the iron and tellurium in two different ways, illustrating how non-equilibrium growth by ALL-MBE provides another route to synthesis that is able to obtain material different from what equilibrium techniques like single crystal growth get. In particular, oxygen leading to superconductivity is interstitial and not chemically bonded to the iron atoms. Under conditions which cause oxygen to substitute for tellurium no superconductivity is found. We have also studied the way in which



Using these growth processes, we have fabricated tunnel junctions to test a prediction by Koshelev that if the order parameter symmetry of the FeTe:O is S± wave, then this should exhibit an unusual proximity effect into a thin adjacent S wave superconductor placed in intimate contact. To do this we made bilayers of FeTe:O with a thin aluminum overlayer. This is followed by a thin Al2O3 barrier layer and capped with a gold layer that acts as a tunnel junction injector. The films have been processed into mesa style devices. Such devices reveal the electronic density of states (DoS) which is proportional to the tunneling conductance. Measurements show a gap in the aluminum DoS that develops below the FeTe:O transition temperature showing that superconductivity in the FeTe:O is able to "leak into" the aluminum film. This suggests that the order parameter symmetry is not S±. However, Koshelev's prediction of specific features in the conductance requires us to test the junctions at temperatures below the superconducting transition temperature of alumimum and preferably significantly below this. We are in the process of doing this now and will report the final results at the meeting.

POSTDOCTORAL RESEARCHER FINALISTS

NEW TERNARY MATERIALS DISCOVERED BY INVERSE DESIGN

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The experimental realization of new inorganic compounds is limited by the large number of possible combinations of elements and the difficulties to identify and structurally characterize the new materials. In this context, the Inverse Design approach greatly accelerated the discovery of missing ABX ternary materials that satisfy the 18-electron valence rule by predicting their stability and crystal structures [1]. Synthesis of the predicted "missing" compounds by arc melting and vacuum annealing of stoichiometric ABX mixtures of pure elements resulted in the identification of TaCoSn [2], TaIrGe, ScRhTe, ZrRhBi, HfIrSb, VIrSi, VRhSi and HfRhP, all eight adopt the crystal structure predicted. Interesting optical and electronic properties were targeted such as for TaIrGe which is a transparent hole conductor.

Experimental realization of these materials demonstrates that theoretical prediction is key to identifying stable missing materials and in providing accurate information about the symmetry of these crystal structures. This latter information is critically important to accelerate the characterization of any newly made phase.

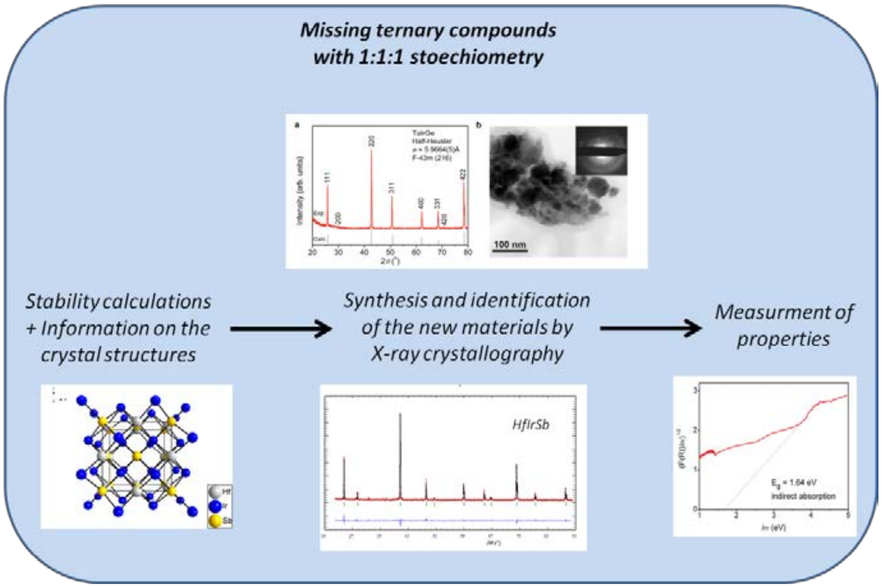

Figure 1. The discovery of missing ABX materials by Inverse Design.

References:
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MICROSTRUCTURAL INVESTIGATIONS OF KR AND XE IRRADIATED UO_2

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Revealing the microstructural damage of nuclear fuels under irradiation is of significance in understanding and modeling the thermal transport in nuclear fuels. In this study, both single-crystal and polycrystalline UO_2 were irradiated with in situ Kr and Xe ions at room temperature and high temperatures. The ion dose dependence of defect microstructure (dislocation loops, dislocations and gas bubbles) was investigated by an in situ transmission electron microscopy (TEM). A dislocation loop denuded zone near the surface and grain boundary indicates they are good sinks for irradiation-induced defects. Interstitial-type dislocation loops with a Burgers vector along <110> were observed in the irradiated UO_2. Further, stoichiometry and gas distribution in the irradiated UO_2 were characterized by atom probe tomography (APT) and electron energy loss spectroscopy (EELS). The stoichiometry of UO_2 is stable during irradiation and the gas distribution shows a similar profile with SRIM calculation but the measured gas content is much lower than the calculated one.

PHOTOTROPIC GROWTH CONTROL OF NANOSCALE PATTERN FORMATION IN PHOTOELECTRODEPOSITED SE–TE FILMS

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Photoresponsive materials that adapt their growth rates dynamically to the local incident electromagnetic field would provide a remarkable route to the synthesis of complex three-dimensional mesoscale structures. Such light-mediated growth processes could enable the design of a variety of energy conversion materials such as self-assembled photonic devices, 3-D electrode architectures, chiral and negative index metamaterials, as well as optoelectronic devices that exhibit wavelength- and polarization-selective photoconductivity. We report the observation of light-mediated growth in an inorganic system and consequently demonstrate the ability to create complex, nanostructured materials via feedback between illumination and the morphology that develops in response to optical excitation. Ordered nanoscale lamellar patterns developed spontaneously in electrodeposited selenium–tellurium (Se–Te) alloy films grown under uniform illumination on unpatterned substrates in an isotropic electrolyte solution. These inorganic nanostructures exhibited phototropic growth in which the lamellar stripes grew towards the incident light source, adopted an orientation parallel to the light polarization direction, and showed an increased growth rate with increasing light intensity (see Figure 1). The illumination wavelength controlled the lamellar period, which varied from 130 nm for ultraviolet light to 412 nm for near-infrared light. Furthermore, the patterns responded dynamically to changes during growth in the polarization, wavelength, and angle of the incident light, enabling the template-free and pattern-free synthesis of woodpile, spiral, branched, or zigzag structures. Full-wave electromagnetic simulations were used to model the absorption profile of nanostructured Se–Te films. To simulate feedback between the local absorption and film growth, an iterative model was used in which the photocarrier generation rate calculated from the electromagnetic simulations controlled the local deposition rate in Monte Carlo simulations of the evolution of the surface. This model reproduced the experimentally observed nanoscale lamellar patterns and also reproduced their dependence on the wavelength and polarization of the incident illumination. The simulations and experiments indicate that phototropic growth is an emergent resonant phenomena that occurs dynamically during film growth in response to the incident illumination conditions, providing the ability to grow structures of entirely different geometries, periods, and directions abruptly on top of one another, and the ability to change the physical growth direction of the material by changing the direction of the incident light beam.

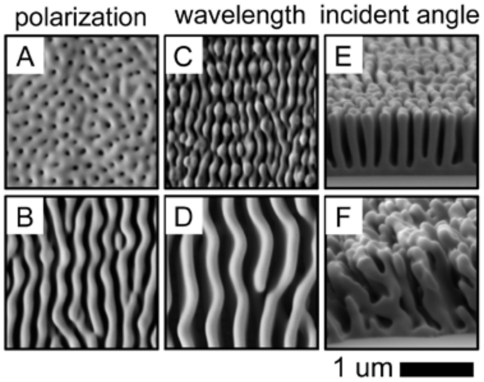

Figure 1. Phototropic growth control of selenium–tellurium films. Nanoscale patterns grown under (A) randomly polarized and (B) linearly polarized, 625 nm illumination. Patterns grown under (C) 405 nm and (D) 940 nm, linearly polarized illumination. Cross-sectional images of patterns grown under (E) normal incident, 625 nm illumination and (F) 625 nm illumination at an angle of 60° from normal.

FIRST-PRINCIPLES STUDIES OF LOSS MECHANISMS IN LIGHT-EMITTING DIODES

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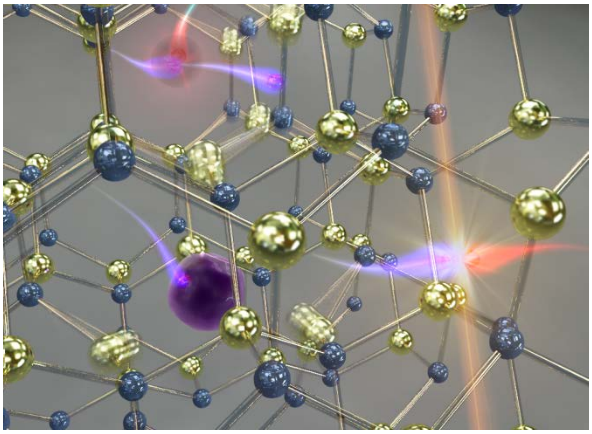
Indium gallium nitride alloys are successfully being used for light emitting diodes (LEDs) in the green to ultraviolet part of the optical spectrum. These devices are the key enablers to Solid-State Lighting, which promises to significantly cut electricity consumption. Applications are still limited, however, by the declining efficiency of LEDs at high currents (“droop”), particularly at longer weavelengths.

Several mechanisms have been suggested as the cause of this efficiency loss, such as Auger recombination and free carrier absorption. Experimentally it is very difficult to discriminate between different nonradiative processes. We have therefore addressed the loss mechanisms based on state-of-the-art first-principles computational theory. We use *ab initio* wave functions and bands that are accurate throughout the entire Brillouin zone (as opposed to **k.p** band structures). Various scattering mechanisms have been taken into account, including scattering by alloying, defects, and phonons. The electron-phonon coupling is explicitly evaluated; this interaction is usually modelled by the Fröhlich expression and this is the first time that the validity of this model is verified from *ab initio* data.

For Auger recombination we find that both electron-electron-hole and hole-hole-electron processes contribute, and that indirect processes assisted by alloy scattering and by electron-phonon coupling dominate. The magnitude of the resulting Auger coefficient indicates that Auger recombination is indeed responsible for the efficiency reduction at high carrier densities.

Calculations for other III-V materials shed light on the microscopic mechanism of this process. Based on simulations of quantum-well structures we also investigate the interplay of polarization fields and Auger recombination in the efficiency droop of nitride light-emitting diodes, pointing to approaches to mitigate the effect of this intrinsic loss mechanism.



Schematic depiction of radiative and nonradiative recombination processes in a nitride crystal. In a radiative process (right), electrons and holes recombine and a photon is emitted. In a defect-assisted nonradiative process (bottom left), an electron is trapped by a defect (here a nitrogen vacancy, represented by a dark wave function). In Auger recombination (top left), an electron and hole recombine but the energy is transferred to a third carrier which is excited to a higher-energy state.

DEVELOPMENT OF *IN SITU* MAGNETIC RESONANCE TECHNIQUES TO STUDY LI METAL BATTERIES AND SUPERCAPACITORS IN REAL TIME

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In situ NMR/ MRI has proven to be a useful tool to probe the structure of Li-ion batteries (LIBs) during real-time charge and discharge[1-4]. *Ex situ* studies of batteries are limited by self-relaxation of the electrode materials before a measurement can be obtained. The application and further development of advanced magnetic resonance techniques *in situ*, such as MRI and complex NMR experiments, has the potential to monitor dynamics and structural changes in functioning electrochemical systems in real time. Here we present *in situ* NMR/ MRI of Li metal batteries and symmetric carbon based supercapacitors.

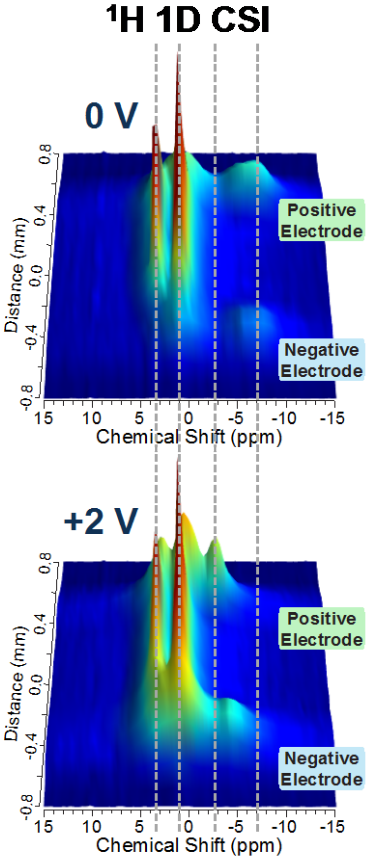

Figure. 1. *In situ* CSI images of an YP17 carbon symmetric supercapacitor at 0V and +2V. Changes in the chemical shift are observed at different voltages indicative of changes in the interaction of the cation with the carbon electrode.

The formation of dendrites on the surface of Li metal poses a serious safety issue and has prevented the mass commercialization of Li metal batteries. To further understand the formation of Li microstructures, *in situ* ^{7}Li NMR/MRI is used. Using chemical shift magnetic resonance imaging (CSI), the spatial information of the MRI image is correlated to the chemical shift information typically associated with NMR allowing both qualitative and quantitative element specific information to be probed *in situ*. This allows the visualization of where specific chemical species are located within the battery. Analysis of the NMR shift and location of the microstructures on the electrodes surface, gives a correlation between the type of microstructure and the NMR shift.

Supercapacitors function based on the separation of the cations and anions of the electrolyte to the negatively and positively charged electrodes, respectively, resulting in the formation of an electrical double layer at the electrode surface. *In situ* NMR studies showed that the anions and cations of the electrolyte in the supercapacitor films are found to be in three different environments[3]. By using CSI we can achieve spatial resolution of each of the different components at the electrode-electrolyte interface providing further insight on the functionality of supercapacitors as depicted in the CSI images in Fig. 1.

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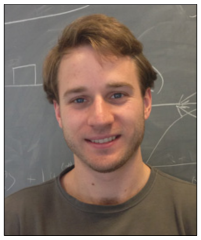

PREDICTING AND UNDERSTANDING THE SINGLET FISSION RATE: A COMBINED THEORETICAL AND EXPERIMENTAL EFFORT

[CE] Shane R. Yost[1], Jiye Lee[2], Mark W. B. Wilson[1], David P. McMahon[1], Rebecca R. Parkhurst[1], Nicholas J. Thompson[2], Akshay Rao[3], Kerr Johnson[3], Matthew Y. Sfeir[4], Moungi Bawendi[1], Timothy M. Swager[1], Richard H. Friend[3], Marc A. Baldo[2], and Troy Van Voorhis[1]

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Exciton fission is a process whereby one singlet exciton splits into two independent triplets. Because fission generates two triplet excitons from a single high energy photon, fission-based solar cells could lead to single junction photovoltaics with power conversion efficiencies above 40%[1]. Here, we measure fission dynamics using ultrafast photoinduced absorption and derive a first principles expression for the singlet fission rate. Our results show that the experimental rates are consistent with a nonadiabatic Marcus-like mechanism in weakly interacting systems and an adiabatic, coupling independent pathway at larger interaction strengths. For a range of electronic couplings covering three orders of magnitude, we predict near unit fission efficiency in any material where fission is energetically favored. This is confirmed experimentally, as we observe high fission yields even in materials where molecules are orthogonally oriented at large separations (>5 Å). We conclude that singlet exciton fission in thin films is robust against variations in molecular structure. The success of this kinetic model simplifies the rational design of fission materials. Crucial molecular properties such as solubility and energy level alignment can be safely tailored by functionalizing an active core while maintaining a high quantum yield.

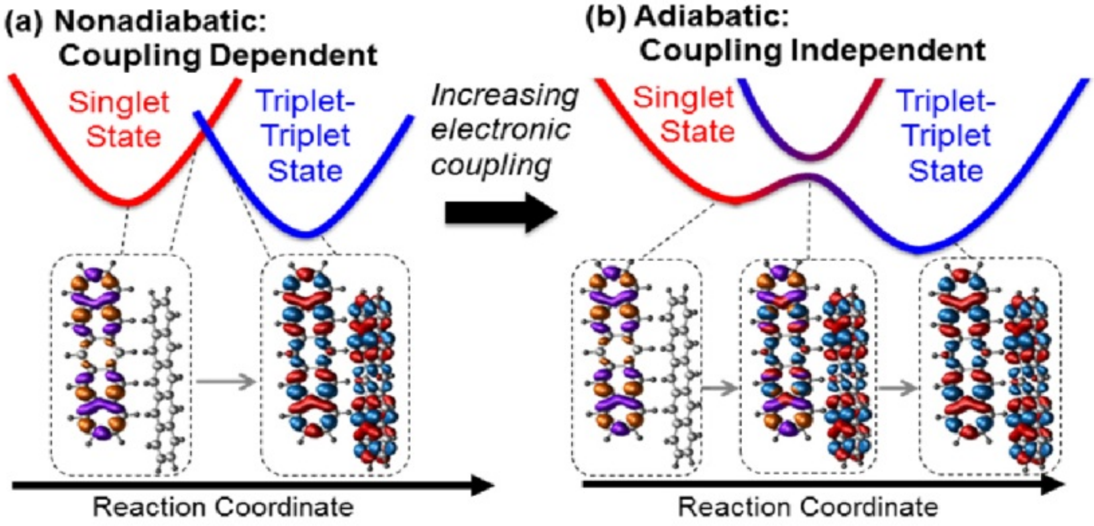

Figure 3. As the coupling between the singlet and triplet-triplet states increases the fission process transitions from nonadiabatic (a) to adiabatic (b) energy transfer. In the nonadiabatic regime transitions between electronic states is abrupt, and the rate is coupling dependent. In the adiabatic case the electronic state changes continuously from singlet to triplet-triplet, and the rate becomes coupling independent.

1. Smith, M. B. & Michl, J. Singlet Fission. *Chemical Reviews* **110**, 6891-6936 (2010).

LIST OF EFRC ACRONYMS

Ordered first by Acronym and then by Director

(ANSER) **Argonne-Northwestern Solar Energy Research Center**
Michael R. Wasielewski, Northwestern University

(BISfuel) **Center for Bio-Inspired Solar Fuel Production**
Devens Gust, Arizona State University

(C3Bio) **Center for Direct Catalytic Conversion of Biomass to Biofuels**
Maureen McCann, Purdue University

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

(CALCD) **Center for Atomic-Level Catalyst Design**
James Spivey, Louisiana State University

(CASP) **Center for Advanced Solar Photophysics**
Victor I. Klimov, Los Alamos National Laboratory

(CCEI) **Catalysis Center for Energy Innovation**
Dion Vlachos, University of Delaware

(CCHF) **Center for Catalytic Hydrocarbon Functionalization**
T. Brent Gunnoe, University of Virginia

(CDP) **Center for Defect Physics in Structural Materials**
G. Malcolm Stocks, Oak Ridge National Laboratory

(CE) **Center for Excitonics**
Marc Baldo, Massachusetts Institute of Technology

(CEEM) **Center for Energy Efficient Materials**
John Bowers, University of California, Santa Barbara

(CEES) **Center for Electrical Energy Storage**
Michael Thackeray, Argonne National Laboratory

(CEFRC) **Combustion Energy Frontier Research Center**
Chung K. Law, Princeton University

(CEN) **Center for Energy Nanoscience**
P. Daniel Dapkus, University of Southern California

(CES) **Center for Emergent Superconductivity**
J. C. Séamus Davis, Brookhaven National Laboratory

(CETM) **Center for Electrocatalysis, Transport Phenomena and Materials for Innovative Energy Storage**
Grigorii Soloveichik, General Electric Global Research

(CFSES) **Center for Frontiers of Subsurface Energy Security**
Steven Bryant, University of Texas at Austin

(CGS) **Center for Gas Separations Relevant to Clean Energy Technologies**
Berend Smit, University of California, Berkeley

(CID) **Center for Inverse Design**
William Tumas, National Renewable Energy Laboratory

(CISSEM) **Center for Interface Science: Solar Electric Materials**
Neal R. Armstrong, University of Arizona

(CLSF) **Center for Lignocellulose Structure and Formation**
Daniel Cosgrove, Pennsylvania State University

(CME) **Center for Molecular Electrocatalysis**
R. Morris Bullock, Pacific Northwest National Laboratory

(CMIME) **Center for Materials at Irradiation and Mechanical Extremes**
Amit Misra, Los Alamos National Laboratory

(CMSNF) **Center for Materials Science of Nuclear Fuel**
Todd Allen, Idaho National Laboratory

(CNEEC) **Center on Nanostructuring for Efficient Energy Conversion**
Stacey Bent and Fritz Prinz, Stanford University

(CST) **Understanding Charge Separation and Transfer at Interfaces in Energy Materials**
Peter J. Rossky, University of Texas at Austin

(CSTEC) **Center for Solar and Thermal Energy Conversion**
Peter F. Green, University of Michigan

(Efree) **Center for Energy Frontier Research in Extreme Environments**
Ho-kwang Mao, Carnegie Institution of Washington

(emc^2) **Energy Materials Center at Cornell**
Héctor D. Abruna, Cornell University

(FIRST) **Fluid Interface Reactions, Structures and Transport Center**
David J. Wesolowski, Oak Ridge National Laboratory

(HeteroFoaM) **Heterogeneous Functional Materials Center**
Kenneth Reifsnider, University of South Carolina

(IACT) **Institute for Atom-efficient Chemical Transformations**
Christopher L. Marshall, Argonne National Laboratory

(LMI) **Light-Material Interactions in Energy Conversion**
Harry Atwater, California Institute of Technology

(MEEM) **Molecularly Engineered Energy Materials**
Vidvuds Ozolins, University of California, Los Angeles

(MSA) **Materials Science of Actinides**
Peter C. Burns, University of Notre Dame

(NCGC) **Center for Nanoscale Control of Geologic CO_2**
Donald J. DePaolo, Lawrence Berkeley National Laboratory

(NECCES) Northeastern Center for Chemical Energy Storage
M. Stanley Whittingham, Stony Brook University

(NEES) Nanostructures for Electrical Energy Storage
Gary Rubloff, University of Maryland

(NERC) Non-equilibrium Energy Research Center
Bartosz A. Grzybowski, Northwestern University

(PARC) Photosynthetic Antenna Frontier Research Center
Robert E. Blankenship, Washington University in St. Louis

(PHaSE) Polymer-Based Materials for Harvesting Solar Energy
Paul Lahti & Thomas Russell, University of Massachusetts, Amherst

(RMSSEC) Revolutionary Materials for Solid State Energy Conversion
Donald T. Morelli, Michigan State University

(RPEMSC) Re-Defining Photovoltaic Efficiency Through Molecule Scale Control
James Yardley, Columbia University

(S3TEC) Solid-State Solar-Thermal Energy Conversion Center
Gang Chen, Massachusetts Institute of Technology

(SSLS) EFRC for Solid State Lighting Science
Michael E. Coltrin, Sandia National Laboratories (NM)

(UNC) Center for Solar Fuels
Thomas J. Meyer, University of North Carolina