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INTRODUCTION TO THE GRADUATE STUDENT AND POSTDOCTORAL RESEARCHER COMPETITION AT THE 2015 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. 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. These integrated, multi-investigator Centers are tackling some of the toughest scientific challenges hampering advances in energy technologies.

EFRC Research Areas

The 32 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 electrical energy storage, solar energy, carbon capture and sequestration, advanced nuclear energy systems, materials under extreme conditions, biosciences, and quantum materials. 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 2015 EFRC Principal Investigators' Meeting

From the 1100 graduate students and postdoctoral researchers involved in the EFRC program, each of the 32 EFRCs was invited to nominate one graduate student and one postdoctoral researcher to present a talk at the 2015 EFRC Principal Investigators' Meeting in Washington, D.C. on October 26-27, 2015. The DOE EFRC management team selected 16 finalists from more than 50 nominations. 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, scientific excellence, and topical diversity. 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

Probing Supercapacitor Carbon-Electrolyte Structure and Ion Dynamics with Neutrons

[FIRST] Boris Dyatkin[1], Hsiu-Wen Wang[2], Eugene Mamontov[3], Naresh Osti[3], Katherine Page[3], Ray Unocic[3], Gernot Rother[3], Matthew Thompson[4], Yu Zhang[4], Peter Cummings[4], David Wesolowski[3], Yury Gogotsi[1]

[1]Drexel University; [2]University of Tennessee; [3]Oak Ridge National Laboratory; [4]Vanderbilt University

Electrochemical capacitors (supercapacitors) showcase high energy and power densities and exhibit exceptional promise in electrical energy storage applications including transportation and grid storage systems. Carbide-derived carbon (CDC) electrodes feature high specific surface areas (> 2000 m^2/g) and narrow porosity distributions (0.7 nm d_{av}) and, as a result, offer optimal capacitances. Although simulations and experimental findings have determined the influence of the ion/pore diameter ratio on charge accumulation, most studies have not investigated the interface between pore surfaces and electrolytes. The influence of surface chemistry and graphitic ordering on capacitance, charge/discharge rates, and electrochemical stability is poorly understood. Furthermore, conventional materials characterization and electrochemical testing approaches are incapable of quantifying essential structural properties and ion dynamics. This insight is vital for the design of the next generation of high-performance supercapacitors.

We present our findings that rely on a combination of neutron scattering and spectroscopy with Quenched Molecular Dynamics (QMD) to correlate structural and chemical features of porous carbons with capacitance and electrosorption dynamics. We used chemical treatments, such as air oxidation and vacuum annealing, to modify graphitization and surface chemistry of nanoporous CDCs derived from SiC and Mo_2C. We relied on neutron diffraction and electron energy loss spectroscopy (EELS) to quantify thermally-driven graphite ring content transformations (5–, 6–, 7–member rings) and prevalent sp^2/sp^3 bonding in CDCs. We used small-angle neutron scattering (SANS) to assess changes in surface roughness and porosities and combined them with Pair Distribution Function (PDF) analysis of X-ray and neutron total scattering data (Fig. 1a) to develop comprehensive structural models of the CDCs. We combined our measurements with computational models to evaluate surface structure, bonding angles, and grain terminations. We filled the pores of differently functionalized CDCs with Room Temperature Ionic Liquid (RTIL) electrolytes and used Quasi-Elastic Neutron Scattering (QENS) and inelastic neutron scattering (INS) to probe the structures of confined ions and their dynamics inside of pores (Fig. 1b). We found that oxygen-rich pores became more ionophilic and showed enhanced mobilities of electrolyte ions, decreased filling densities, and lowered vibrational energies under pore-confinement. We found corresponding improvements in capacitance, higher ion mobility, and lower ionic resistance of electrolytes in oxidized CDCs. We relied on X-Ray PDF analysis to show ion-ion

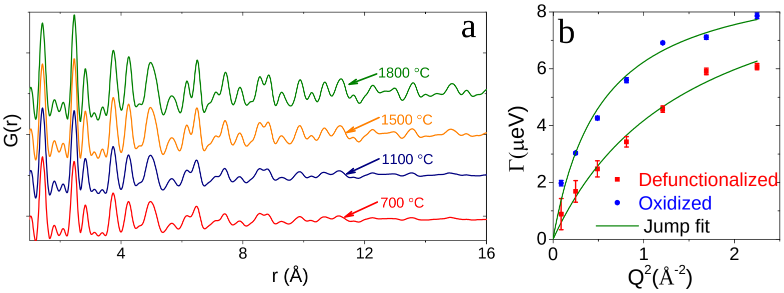


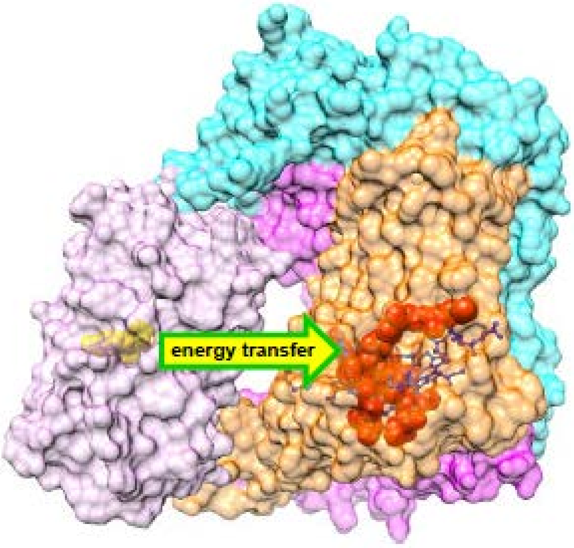
Fig. 1. a) PDF analysis of graphitization and ring prevalence transformations in SiC-CDCs annealed at 700 – 1800 ºC under 10^{-6} torr. b) Cole-Cole fit of energy transfer coefficients of mobilities of $[Omim^+][TF_2N^-]$ RTIL inside of differently functionalized pores of Mo_2C-CDC collected using QENS.

correlation changes and intermolecular interactions confined in defunctionalized vs. oxidized pores. We combined this analysis with MD simulations of electrolyte interactions with functionalized electrode surfaces to correlate electrosorption densities and ion orientations with capacitance and energy densities of these systems.

EXPANDING THE RANGE OF LIGHT ABSORBERS FOR BACTERIAL PHOTOSYNTHESIS: YFP-ENHANCED CHARGE SEPARATION AT THE RHODOBACTER SPHAEROIDES REACTION CENTRE

[PARC] Kaitlyn M. Faries[1], Katie J. Grayson[2], Pu Qian[2], Preston Dilbeck[1], Elizabeth Martin[2], Jonathan M. Yuen[1], Dariusz M. Niedzwiedzki[3], Dewey Holten[1], Christine Kirmaier[1] and C. Neil Hunter[2]

[1]Dept. Chemistry, Washington University, St. Louis; *[2]Dept. Molecular Biology and Biotechnology, University of Sheffield, UK*; *[3]Photosynthetic Antenna Research Center, Washington University, St. Louis*



Idealized schematic model of the Rb. sphaeroides *RC with polypeptide subunits H (cyan), M (magenta) and L (cyan) and pigments (orange/purple) plus attached YFP with protein (light pink) and integral pigment (yellow).*

Native light-harvesting systems of photosynthetic organisms are very efficient at light collection and transfer of energy to a reaction centre (RC) for conversion to chemical energy via charge separation across a membrane. However, that efficiency is often limited to certain color ranges of solar light because of gaps in the visible and near-infrared spectrum where the antenna pigments do not absorb. Although incorporation of synthetic chromophores to complement the absorption spectrum of native light-harvesting proteins in biohybrid architectures is promising, the approach is challenging and generally involves pigment integration post purification of proteins from the organism and *in vitro* assembly. However, fluorescent proteins such as green fluorescence protein (GFP) and derivatives offer the advantage of *in vivo* incorporation and production. In this study, we incorporated a yellow fluorescent protein (YFP) derivative (sYFP2) gene at the C-terminus of the gene for the H-polypeptide subunit of the RC in the purple photosynthetic bacterium *Rhodobacter sphaeroides*. The engineered organism grows photosynthetically. The strong YFP emission has excellent spectral overlap with the visible-region (Q_X) absorption bands of the RC, allowing for energy transfer from YFP to RC via a long-range dipole-dipole trough- space (Förster) mechanism. We used a number of complementary static and ultrafast time-resolved absorption and fluorescence techniques to quantify the yield of energy transfer from YFP to the RC, which was found to $\Phi_{EET} = 0.4 \pm 0.1$. Using Förster theory, including the YFP emission and RC absorption spectral overlap, a Förster radius R_0 (distance at which $\Phi_{EET} = 0.5$) of 55 Å was obtained for the YFP/RC energy donor/acceptor pair. The values $\Phi_{EET} = 0.4$ and $R_0 = 55$ Å give an estimated distance between the YFP and RC pigments of R = 60 Å. This work demonstrates the viability of incorporating fluorescent proteins into the genome of photosynthetic systems to complement production of their existing suite of light-harvesting proteins and chromophores, thereby conferring new capabilities on the native organisms.

INCORPORATION OF PERYLENE-3,4-DICARBOXIMIDES INTO PHOTOANODES AND PHOTOCATHODES FOR SOLAR FUELS

[ANSER] Rebecca J. Lindquist[1], Marek B. Majewski[1], Julianne M. Thomsen[2], William L. Hoffeditz[1], Brian T. Phelan[1], Kelly L. Materna[2], Joseph T. Hupp[1], Gary W. Brudvig[2], Michael R. Wasielewski[1]

[1] Department of Chemistry, Northwestern University; [2]Department of Chemistry, Yale University

The rational design of efficient photoelectrochemical cells (PECs) for the production of fuels using solar energy will require an understanding of the catalytic mechanisms and rate-limiting steps of photodriven water oxidation and fuel-forming reactions. Perylene-3,4-dicarboximide (PMI) chromophores are promising candidates for incorporation into PECs and for the mechanistic investigation of these processes by ultrafast spectroscopic techniques due to their synthetic tunability, strong absorptivity in the midvisible spectral region, and distinctive spectral features. We have previously used femtosecond to millisecond transient absorption spectroscopies to identify a PMI derivative capable of injecting electrons into nanostructured TiO_2 films and oxidizing a covalently attached homogeneous water oxidation catalyst (WOC) precursor Cp*Ir^{III}(ppy)Cl, where ppy = 2-phenylpyridine,[1,2] following photoexcitation.[3] We now incorporate PMI into several photoelectrodes for the photodriven oxidation and reduction of solar fuels catalysts. The TiO_2-based photoanodes contain a coadsorbed WOC $[(Ir^{IV}(\text{pyalc})(H_2O)R)_2(\mu\text{-}O)]^{+2}$, where pyalc = 2-(2′pyridyl)-2-propanolate,[4] or a heterogeneous cobalt oxide (Co-Pi) WOC.[5] Photocathodes include molecular $[Ni(P^2N^2)_2]^{2+}$-based proton reduction catalysts[6] on nanostructured NiO. Atomic layer deposition of Al_2O_3 following chromophore adsorption[7] was employed to improve the chemical stability of the chromophores and to prevent rapid electron-hole recombination. Photoelectrochemical experiments and ultrafast optical spectroscopies were used to probe the photocatalytic activities and photodriven electron transfer events of the photoelectrodes.

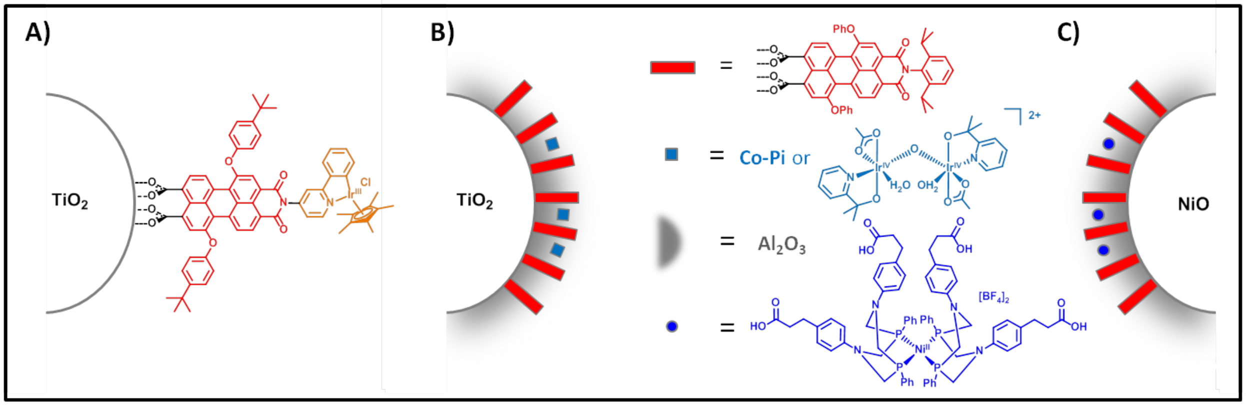


Fig.1 – Designs of model TiO_2/PMI-Cp*Ir^{III}(ppy)Cl (**A**) and TiO_2/PMI/Al_2O_3/Co-Pi or $[(Ir^{IV}(\text{pyalc})(H_2O)R)_2(\mu\text{-}O)]^{+2}$ (**B**) photoanodes and NiO/PMI/Al_2O_3/$[Ni(P^2N^2)_2]^{2+}$ photocathodes (**C**).

[1] J. D. Blakemore, G. W. Brudvig, R. H. Crabtree, *et al. J. Am. Chem. Soc.* **132**, 16017-16029 (2010). [2] M. T. Vagnini, L. X. Chen, M. R. Wasielewski, *et al. Chem. Sci.* **4**, 3863-3873 (2013). [3] R. J. Lindquist, B. T. Phelan, J. R. Durrant, M. R. Wasielewski, *et al. Submitted.* [4] S. W. Sheehan, J. M. Thomsen, R. H. Crabtree, G. W. Brudvig, C. A. Schmuttenmaer, *et al. Nat. Commun.* **6**, 6469 (2015). [5] M. W. Kanan, D. G. Nocera, *Science* **321**, 1072-1075 (2008). [6] U. J. Kilgore, R. M. Bullock, D. L. DuBois, *et al. J. Am. Chem. Soc.* **133**, 5861-5872 (2011). [7] H.-J. Son, O. K. Farha, J. T. Hupp, *J. Am. Chem. Soc.* **135**, 11529-11532 (2013).

POSTDOCTORAL RESEARCHER WINNERS

THE ROLE OF ADVANCED REACTIVE SURFACE AREA CHARACTERIZATION IN IMPROVING PREDICTIONS OF MINERAL REACTION RATES IN SUBSURFACE POROUS MEDIA

[NCGC] Lauren E. Beckingham[1], Elizabeth Mitnick[2], Carl I. Steefel[1], Shuo Zhang[2], Li Yang[1], Marco Voltolini[1], Alexander M. Swift[3], David R. Cole[3], Julie M. Sheets[3], Timothy Kneafsey[1], Gautier Landrot[4], Lawrence Anovitz[5], Saeko Mito[6], Ziqiu Xue[6], Donald DePaolo[1,2], Jonathan Ajo-Franklin[1]

[1]Lawrence Berkeley National Laboratory; [2]University of California, Berkeley; [3]Ohio State University; [4]Synchrotron SOLEIL; [5]Oak Ridge National Laboratory; [6]Research Institute of Innovative Technology for the Earth (RITE)

Mineral reaction rates remain difficult to predict as numerous uncertainties and imprecisions exist in current mineral dissolution and precipitation modeling capabilities. One of the major uncertainties arises from a lack of understanding of mineral reactive surface area. Common estimates of mineral reactive surface area are ad hoc and typically based on grain size, adjusted several orders of magnitude to account for surface roughness and reactivity. This results in orders of magnitude discrepancies in estimated mineral reactive surface area that directly translate into orders of magnitude discrepancies in model predictions. Additionally, natural systems can be highly heterogeneous and contain abundant nano- and micro-porosity, which can limit connected porosity and access to mineral surfaces. In this study, mineral-specific accessible surface areas are computed for a sample from the reservoir formation at the Nagaoka pilot CO_2 injection site (Japan). Accessible mineral surface areas are determined from a multi-scale image analysis including X-ray microCT, SEM QEMSCAN, XRD, SANS, and SEM-FIB. These estimates not only account for accessibility of mineral surfaces to macro-pores, but accessibility through nano-pores, especially important given the abundance of mineral surfaces coated by porous smectite in this sample. Powder and flow-through column laboratory experiments are performed and the evolution of solutes in the aqueous phase is tracked. Continuum-scale reactive transport models are used to evaluate the impact of reactive surface area on predictions of experimental reaction rates. Evaluated reactive surface areas include geometric and specific surface areas (eg. BET) in addition to their reactive-site weighted counterparts. The most accurate predictions of observed powder mineral dissolution rates were obtained through use of grain-size specific surface areas computed from a BET-based correlation. Effectively, this surface area reflects the grain-fluid contact area, or accessible surface area, in the powder dissolution experiment. In the model of the flow-through column experiment, the accessible mineral surface area, computed from the multi-scale image analysis, is evaluated in addition to the traditional surface area estimates.

PREDICTING AND CONTROLLING POLYMORPHISM IN TRANSITION METAL OXIDES

[CNGMD] Lauren M. Garten[1], Hong Kevin Ding[2], Laura T. Schelhas[3], Kevin Stone[3], Prashun Gorai[1], Paul Ndione[1], Kristin Persson[2], Michael F. Toney[3], Vladan Stevanović[1,4], David S. Ginley[1]
[1]National Renewable Energy Laboratory; [2]Lawrence Berkeley National Laboratory; [3]SSRL Materials Science Division, SLAC National Accelerator Laboratory; [4]Colorado School of Mines

Computational materials design is accelerating the development of technologically relevant materials but, in fact, many materials currently in applications are actually kinetically stabilized (i.e. metastable), thus motivating the CNGMD EFRC to address how metastability can be incorporated computationally. Polymorphism (i.e. different energy structures with the same composition) is a key form of metastability and we seek the ability to synthesize a specific functional polymorph from a set of structures close in energy. We report on a new predictive model describing the energy manifold of polymorphic families. This couples to a computational geometric model to identify substrates for growth of specific polymorphs and ultimately to incorporating both surface energy and kinetics.

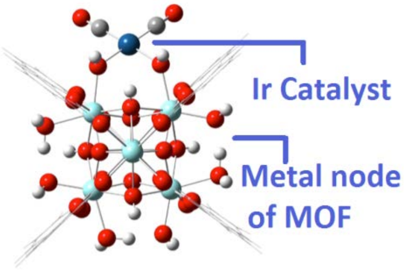
Vanadium oxide, VO_2, was chosen as a model system for computation and experiment due to its extensive polymorphism and relevant electronic functionality. Metastable phases of VO_2 (analogous to the Brookite and Columbite polymorphs of TiO_2) are predicted to form within 15 kJ/mol of the ground state but have not been experimentally observed.[1] Epitaxial stabilization of these phases would establish how far above the convex hull substrate templating can be effective and how accessible are novel phases of a complex correlated material. A computational approach to lattice geometry was developed to target polymorphs. The selection boundary conditions limit the two-dimensional strain to less than 9% and the coincident lattice area to less than 1000 Å. TiO_2-Anatase, TiO_2-Brookite, $SrTiO_3$, and $LaAlO_3$ were identified through this modeling as candidates for the stabilization of VO_2 polymorphs. Pulsed Laser Deposition (PLD) was employed to simultaneously deposit on an array of substrates under identical processing parameters. Varying the substrate, under the same processing conditions, did indeed lead to the formation of different polymorphs. Further, TiO_2-Anatase was correctly predicated to stabilize the metastable A VO_2 phase which lies 70 meV/atom above the convex hull and TiO_2-Brookite was predicated to produce a Brookite VO_2 phase, but rather stabilized the high temperature rutile phase of VO_2. The resulting films indicate that the metal-insulator transition was successfully suppressed to below room temperature in these polymorphs. To further build upon this geometric model, the impact of the deposition kinetics on the phase formation in VO_2 was investigated. Amorphous VO_2 films were deposited under varying laser frequency during PLD. *In-situ* synchrotron x-ray diffraction during rapid thermal annealing and traditional annealing indicated variations in the final phase formation due to initial structural differences in films deposited at different frequencies, providing additional insight into the kinetic pathways for phase formation in VO_2.

[1] Mehta, P., Salvador, P. A., and Kitchin, J. R., *Identifying Potential BO2 Oxide Polymorphs for Epitaxial Growth Candidates.* ACS Applied Materials & Interfaces, 2014. **6**(5): p. 3630-3639.

METAL-ORGANIC FRAMEWORK NODES AS NEARLY IDEAL SUPPORTS FOR MOLECULAR CATALYSTS: NU-1000- AND UIO-66-SUPPORTED IRIDIUM COMPLEXES FOR ETHYLENE HYDROGENATION AND DIMERIZATION

[ICDC] Samuel O. Odoh[1], Dong Yang[2], Timothy Wang[3], Omar K. Farha[3], Joseph T. Hupp[3], Christopher Cramer[1], Bruce C. Gates[2], Laura Gagliardi[1]

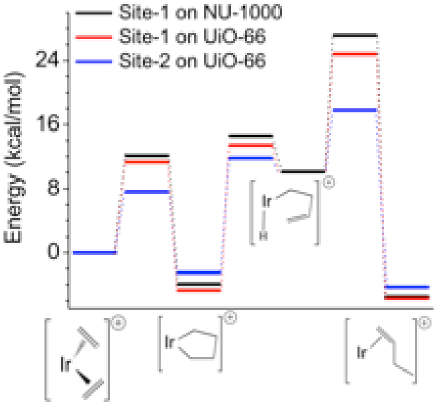
[1]*Department of Chemistry, Chemical Theory Center, and Supercomputing Institute, University of Minnesota*; [2]*Department of Chemical Engineering & Materials Science, University of California, Davis*; [3]*Departments of Chemistry and Chemical and Biological Engineering, Northwestern University*



Iridium sites at the Zr6 nodes of NU-1000.

The Inorganometallic Catalyst Design Center (ICDC) guides the discovery of supported cluster catalysts by integrating computational modeling with experiments in pristine systems that are amenable to high-throughput search and discovery methods. Metal-organic frameworks (MOF) with Zr_6 nodes, UiO-66 and NU-1000, were investigated as supports for $Ir(CO)_2$ and $Ir(C_2H_4)_2$ complexes. Quantum chemical calculations based on density functional theory (DFT) were employed to explore the local structure of the Ir-based catalysts at the MOF nodes, the number and nature of sites in each MOF. They provided results that are in good agreement with infrared and X-ray absorption fine structure spectra.

DFT calculations were also employed to investigate the mechanism for ethylene dimerization and hydrogenation at different catalytic sites. The reactivity of node-supported $Ir(CO)_2$ with C_2H_4 and the catalytic activity and selectivity of the species initially present as $Ir(C_2H_4)_2$ for ethylene hydrogenation and dimerization are affected by the node. We are currently performing DFT computations to show that the catalytic activity of Ir species deposited in the NU-1000 MOF can be improved by pre-treating this MOF with aluminum. In this case, the Lewis acidity of the aluminumlayer modifies the Ir sites, and thereby modulates the catalytic pathway of ethylene dimerization.



Calculated mechanism for ethylene dimerization at the Iridium sites deposited on MOF nodes.

Reference: Yang D., Odoh S. O., Wang, T.C., Farha O. J., Hupp J., Cramer, C. J., Gagliardi L., Gates B. C., "Metal-organic framework nodes as nearly ideal supports for molecular catalysts: NU-1000- and UiO-66-supported iridium complexes" *J. Am. Chem. Soc.* **2015**, 137, 7391.

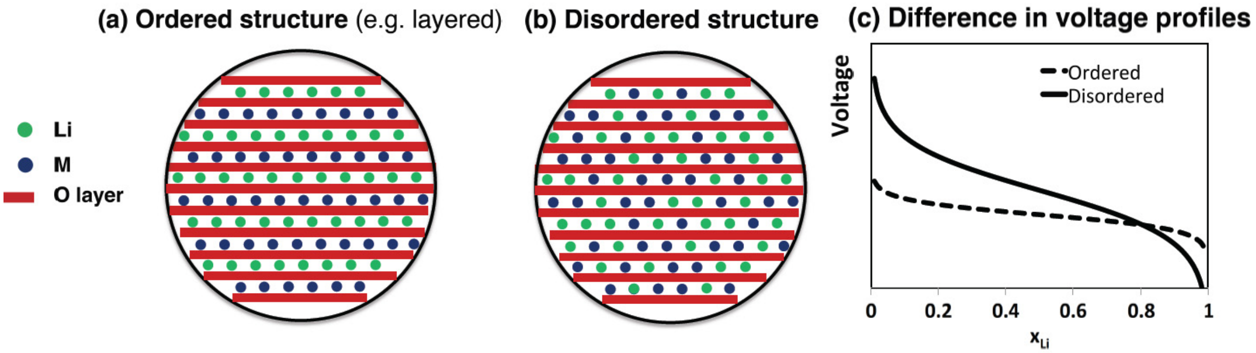
GRADUATE STUDENT FINALISTS

THE EFFECT OF CATION DISORDER ON THE LI INTERCALATION VOLTAGE OF TRANSITION METAL OXIDES

[NECCES] Aziz Abdellahi[1], Alexander Urban[2], Stephen Dacek[1], ShinYoung Kang[1], Pinaki Mukherjee[3], Khim Karki[4], Frederic Cosandey[3], Gerbrand Ceder[2]
[1]Masschusetts Institute of Technology, [2]UC Berkeley [3]Rutgers University, [4]Brookhaven National Laboratory

Cation disorder is a phenomenon that is becoming increasingly important in the field of Li-ion batteries. Disordered Li-excess rocksalts have achieved high-capacity via Li transport through percolating zero-transition-metal pathways[1], paving the way towards a new design space of high-capacity Li-ion battery cathodes. In situ cation-disorder also occurs in a large class of ordered materials, resulting in the formation of disordered bulk or surface phases upon cycling. In particular, commercially relevant NCA ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) particles were shown to undergo surface changes upon delithiation, leading to the formation of disordered rocksalt regions and partially disordered spinel regions at the surface, both with an increased transition metal (TM) to Li ratio [2].

In these cases, cation disorder has a strong impact on the voltage profile of lithium transition metal oxides; altering the average voltage of the Li-intercalation reaction as well as increasing the slope of the voltage profile. Even when cation disorder is limited to the particle surface (such as in the case of NCA), slow Li transport at the disordered surface (which does not have percolating zero-TM pathways) can lead to a voltage profile dominated by the surface redox processes.



In this work, we use first principles methods to understand and quantify the effect of cation-disorder on the Li-insertion voltage of transition metal oxides. In order to isolate the effect of cation-disorder from other effects such as the of Li/TM ratio, we investigate the effect of cation-disorder on the voltage of *stoichiometric* transition metal oxides. Our first principles work is complemented by detailed TEM characterization of NCA surfaces, thus helping clarify the structure and composition of the (partially) disordered phases that form at the surface.

[1] Lee et al., Science, 2014. [2] Hwang et al., *Chemistry of Materials*, 2015.

REVEALING THE SUGAR ISOMERIZATION MECHANISM ON HOMOGENEOUS SN-SILICATE CATALYSTS

[CCEI] Tyler Josephson[1], Kramer Brand[2], Jay Labinger[2], Mark Davis[2], Dion Vlachos[1], Stavros Caratzoulas[1]
[1]University of Delaware, [2]California Institute of Technology

The isomerization of glucose to fructose has recently emerged as an important route for the conversion of cellulose to intermediate platforms.[1] Sn-Beta zeolite catalyst has been active for transforming glucose into its isomer fructose, as well as its epimer mannose.[2] The active sites in these heterogeneous materials are difficult to characterize, especially under reaction conditions.[3,4] We developed a homogeneous catalyst model to isolate, characterize and test different types of active sites, and compare these to heterogeneous catalysts. These stannasilsequioxane catalysts, or Sn-Cubes, are active for glucose isomerization and epimerization, although they differ in selectivity from Sn-Beta.

In conjunction with experimental work, we performed electronic structure calculations to investigate numerous isomerization and epimerization pathways on this Sn-Cube catalyst. We modelled the full catalytic cycle, including ring-opening of glucose, hydride transfer and Bilik reactions to form fructose and mannose, and ring-closing of these products. The complete reaction network was analyzed using the energetic span model to estimate the relative rates of isomerization and epimerization. We found agreement between our predictions and kinetic measurements, as well as ^{13}C labelling experiments that distinguish among the different possible pathways for producing fructose and mannose.

The properties of these Sn-Cubes are compared to those of Sn-Beta in order to close the gap between molecular analogues of a heterogeneous catalyst and the actual material. A key feature of the active open site in Sn-Beta is the stannanol group which facilitates proton transfers in ring-opening and ring closing reactions, and a silanol group which facilitates the hydride transfer reaction steps.[2,5] These Sn-Cubes have an inert methyl group in place of a stannanol, but this does not preclude them from catalyzing this reaction. Instead, ring-opening and ring-closing are facilitated via a Sn-O-Si bridge, which accepts a proton from a glucose hydroxyl, breaks the bridge, and forms a silanol, which can participate in later reactions as the Sn-Beta open site silanol does. In addition, while the Sn-Cubes deactivate when exposed to water, the zeolite framework in Sn-Beta stabilizes the open site, preventing deactivation.

[1] Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. *Green Chem.* **2010**, *12*, 1493.
[2] Bermejo-Deval, R.; Assary, R. S.; Nikolla, E.; Moliner, M.; Roman-Leshkov, Y.; Hwang, S.-J.; Palsdottir, A.; Silverman, D.; Lobo, R. F.; Curtiss, L. a.; Davis, M. E. *Proc. Natl. Acad. Sci.* **2012**, *109* (25), 9727–9732.
[3] Bermejo-Deval, R.; Orazov, M.; Gounder, R.; Hwang, S. J.; Davis, M. E. *ACS Catal.* **2014**, *4* (7), 2288–2297.
[4] Bermejo-Deval, R.; Gounder, R.; Davis, M. E. *ACS Catal.* **2012**, *2* (12), 2705–2713.
[5] Rai, N.; Caratzoulas, S.; Vlachos, D. G. *ACS Catal.* **2013**, *3* (10), 2294–2298.

UNDERSTANDING AND IMPROVING THE CHEMISTRY OF LEAD CHALCOGENIDE QUANTUM DOTS FOR PHOTOVOLTAICS

[CASP] Ashley R. Marshall[1,2], Arthur J. Nozik[2], Matthew C. Beard[1], Joseph M. Luther[1]
[1]*National Renewable Energy Laboratory;* [2] *University of Colorado*

We are exploring the surface and defect chemistry of lead sulfide (PbS) and lead selenide (PbSe) quantum dots (QDs) to more effectively utilize multiple exciton generation (MEG) for next generation solar cells. Synthetic routes to PbS or PbSe QDs formerly involved PbO as a precursor, however new findings suggest that lead halide precursors produce "better" QDs. Diffusion-based syntheses *and* cation exchange syntheses using Pb-halides produce QDs with improved carrier transport, improved MEG efficiency, and better air stability due to halide incorporation from the precursor. Thus, understanding the role that the synthetic route plays in the photophysical properties of QD films is of timely interest.

To transition isolated, soluble QDs into a macroscopic semiconducting film (a "QD solid") for photovoltaic (PV) devices, for example, a solid-state surface ligand exchange replaces insulating long chain ligands with short molecular ligands and brings the QDs in close proximity for electronic transport. However, the treatment scheme can also add or exchange atoms on the surface or reassemble the surface configuration. Using these tools to control the surface, we are able to improve the photoluminescence characteristics and device performance of QD solids.

Photoluminescence (PL) studies on QDs synthesized from PbO have shown that temperature dependent PL quenching is a metric of the defect properties in a QD solid; PL is strong at low temperatures, but quenches as the film heats, due to free carriers moving to defect sites and recombining nonradiatively. Using halide syntheses, PbS QD solids show bimolecular, radiative recombination at room temperature (inset of Figure 1B). Persistent PL at room temperature suggests that these QDs have fewer trap states and can produce higher open circuit voltage in PV devices.

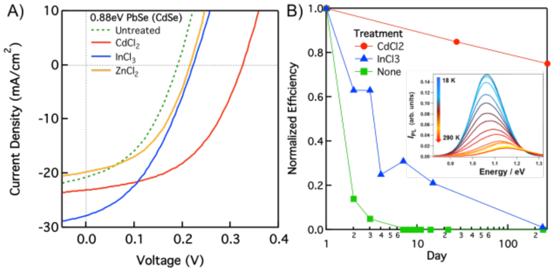


Figure 2: (A) *J-V* curves for PbSe QD solar cells with a selection of metal chloride treatments. (B) Plot of normalized efficiency over time; the CdCl2 treatment gives over 270 days of stability stored in air. Inset: temperature dependent PL for a PbS QD solid.

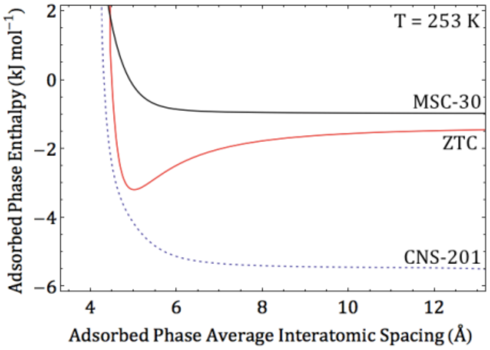
PV devices with remarkable efficiency were fabricated with these halide-synthesized PbS and PbSe QDs and show increased open circuit voltage (*Voc*). Furthermore these air-stable QDs give record efficiency devices (fabricated/stored in air) and were used for the first certified PbSe QD PV device. We explored how the uptake of metal chloride species into QD films influences device performance parameters (Figure 1A). We are able to tune either the short circuit current (J_{sc}) or V_{OC} in the device by choice of metal cation and devices treated with $CdCl_2$ show excellent resistance to degradation (Figure 1B).

While speculations on the surface of lead chalcogenide QDs is central to many of the papers proposing new ligands and treatments for QDs, very little work has been done to elucidate the chemistry at the QD surface. Using a combination of analytic and organic chemistry techniques, we probe the surface and composition of the QDs. We compare the QDs as a function of the synthesis route to determine why the new QDs show better properties. We also study the native ligands and ligand exchange processes using NMR, FTIR, and elemental analysis. Using all of these techniques in conjunction enables a comprehensive picture of the QD and the surface chemistry involved in making QD solids for optoelectronic devices.

ANOMALOUS SURFACE THERMODYNAMICS OF GAS ADSORPTION ON ZEOLITE-TEMPLATED CARBON

[EFree] Maxwell Murialdo, Nicholas P. Stadie, Channing C. Ahn, Brent Fultz
California Institute of Technology

In this talk I will discuss a newly discovered effect in the field of gas adsorption and its impact on three energy-relevant gases: methane, ethane and krypton. While krypton separation (from xenon) is of critical importance to establishing "closed" nuclear fuel cycles, methane and ethane are the main components in natural gas. For natural gas-fueled cars, the ability to store the necessary quantities of natural gas in inexpensive and moderately sized onboard tanks remains a significant challenge. By filling the onboard tanks with specially designed physisorptive materials, the onboard storage capacity can be significantly improved. In particular we have synthesized a zeolite-templated carbon that is one of the best carbonaceous adsorbents for methane storage to date, yielding roughly a 50% improvement over compression alone at room temperature and 90 bars pressure.



While the adsorbed phase enthalpies on conventional carbons (MSC-30 and CNS-201) decrease monotonically with interatomic spacing, on zeolite-templated carbon it resembles a 12-6 Lennard-Jones potential, showcasing the enhanced adsorbate-adsorbate interactions.

Unlike conventional adsorbate-adsorbent systems which have isosteric enthalpies of adsorption that decrease with surface loading, our zeolite-templated carbon has isosteric enthalpies for methane, ethane and krypton adsorption that increase with surface loading [1-3]. The uniquely ordered nanostructure of our zeolite-templated carbon [4] promotes lateral interactions between the adsorbate molecules leading to this anomalous effect. By using a controlled adsorbent nanostructure to thus tune the adsorption thermodynamics, gas storage and separation properties may be favorably modified. Furthermore, to gain a better understanding of this phenomenon, we have developed more robust fitting techniques, and have used statistical mechanical estimates to corroborate our findings and develop a cooperative interaction model of the effect. These techniques are also applicable to the analysis of other adsorbents and may prove useful for understanding adsorption properties on other carbons that have been synthesized at high pressures by EFree collaborators in the Lehigh group.

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[3] N.P. Stadie, M. Murialdo, C.C. Ahn, and B. Fultz, "Anomalous Isosteric Enthalpy of Adsorption of Methane on Zeolite-Templated Carbon," *J. Am. Chem. Soc*. **135**, 990 (2013).
[4] N.P. Stadie, B. Fultz, C.C. Ahn, and M. Murialdo, "Nanostructured Carbon Materials for Adsorption of Methane and Other Gases," **U.S. Patent 9,067,848.** Jun. 30, 2015.

STRUCTURAL EVOLUTION OF URANYL PEROXIDE NANO-CAGE FULLERENE: U60, AT ELEVATED PRESSURES

[MSA] Katlyn M. Turner[1], Yu Lin[1], Fuxiang Zhang[2], Brendan T. McGrail[3], Wendy Mao[1], Peter C. Burns[3], Rodney C. Ewing[1]

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U60 is a uranyl peroxide nano-cage that adopts a highly symmetric fullerene topology. The topological isomer of U60 is the same as C60 buckminsterfullerene. Several studies on the aqueous-phase of U60 clusters, $[UO_2(O_2)(OH)]_{60}^{60-}$, have shown the persistence and stability of the compound in complex solutions[1] and over lengthy time scales. U60 (Fm-3) crystallizes at ambient conditions with approximate formula: $Li_{68}K_{12}(OH)_{20}[UO_2(O_2)(OH)]_{60}(H_2O)_{310}$. In this investigation, we have used the diamond anvil cell (DAC) to examine U60 *in situ* in order to understand the stability of this cluster at high pressures. We used a symmetric DAC with 300 μm culet diamonds and two different pressure-transmitting media: a 4:1 mixture of methanol + ethanol and silicone oil. By using a combination of *in situ* Raman spectroscopy and synchrotron powder x-ray diffraction (XRD), and electrospray ionization mass spectroscopy (ESI-MS) *ex situ*, we have determined the pressure-induced evolution of the U60 cluster. Crystalline U60 undergoes an irreversible phase transition to a tetragonal structure at 4.1-4.4 GPa, and irreversibly amorphizes between 11-14 GPa. This amorphous phase likely consists of clusters of U60. Above pressures of ~15 GPa, the U60 nano-cage is irreversibly destroyed—ESI-MS shows that this phase consists of several species that likely have between 10-20 uranium atoms. The Raman spectroscopy of crystalline U60 shows two dominant modes[2]: a symmetric stretch of the uranyl U-O triple bond at ~810 cm^{-1}, and a symmetric stretch of the $U-O_2-U$ peroxide bond at ~820-850 cm^{-1}. As pressure is increased, these two modes shift to increasing wavenumbers, and eventually overlap at ~4 GPa. At ~15 GPa, the intensity of these modes decreases below detection. These vibrational results complement the synchrotron XRD measurements. U60 degrades quickly in methanol and ethanol mixtures, as evidenced by broad, diffuse diffraction patterns even at low pressures, however, in silicone oil, crystalline U60 remains intact for several hours. In both studies, a phase transition was observed at 4 GPa. In methanol and ethanol, U60 amorphizes between 10-13 GPa, but in silicone oil, the amorphization pressure is slightly higher: 13-14 GPa. In both studies, the phase transition and amorphization were irreversible. These experiments reveal several novel behaviors: U60 undergoes irreversible phase transitions, the tetragonal phase of U60 is exclusively a high-pressure phase, and the amorphization of the U60 compound occurs before the collapse of the U60 cluster topology. Notably, this is different from the behavior of solvated C60 with increasing pressure, which maintains a hexagonal structure at high pressure (up to 30 GPa), while the clusters become disordered[3]. These results suggest that uranyl nano-cage clusters may be very persistent once formed, regardless of the state of the cluster—crystalline, amorphous, or even in solution.

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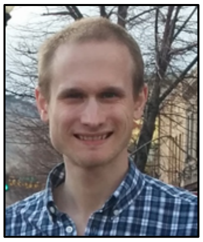
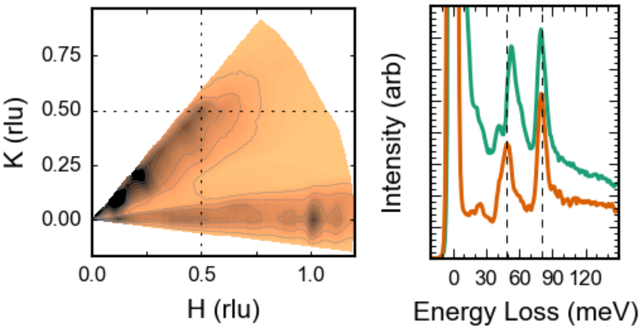


CHARACTERIZATION OF THE LOW-ENERGY BOSONIC MODES IN $Bi_2Sr_2CaCu_2O_{8+x}$ WITH INCIPIENT CHARGE ORDER

[CES] Sean Vig[1], Anshul Kogar[1], Vivek Mishra[2], Luke Venema[1], Melinda S. Rak[1], Ali A. Husain[1], Genda D. Gu[3], Eduardo Fradkin[1], Mike R. Norman[2], Peter Abbamonte[1,2]
[1]*Department of Physics and Materials Research Laboratory, University of Illinois*; [2]*Materials Science Division, Argonne National Laboratory*; [3]*Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory*

Efficiently engineering novel and useful superconducting materials requires an understanding of the mechanism responsible for high-temperature superconductivity and its relation to other emergent phenomena. Though cuprate high-temperature superconductors have been studied intensely for the past 30 years, understanding the mechanism responsible for superconductivity remains a significant challenge in condensed matter physics. Developing this understanding requires knowledge of both the fermionic charge excitations and many-body bosonic interactions that drive the associated emergent phenomena. Much of our current understanding of cuprate superconductors has come from probing fermionic charge degrees of freedom at meV energy scales, which is the energy scale relevant to understanding high-temperature superconductivity and the various collective phases, such as charge order, that compete with it. This mapping has been done both in reciprocal space, with angle-resolved photoemission spectroscopy (ARPES), and in real space, with scanning tunneling spectroscopy (STS). Both of these techniques are able to measure the single particle spectra over several Brillouin zones. However, there is no comparable probe of the bosonic charge degrees of freedom, parameterized by the dynamic susceptibility, $\chi(\mathbf{q},\omega)$. Through work done in the Center for Emergent Superconductivity (CES), we have developed the technique of momentum-resolved electron energy-loss spectroscopy (M-EELS). M-EELS is capable of performing a full momentum-space mapping of the low-energy bosonic degrees of freedom over the first Brillouin zone with meV energy resolution, allowing us to characterize the interactions that give rise to collective electron dynamics. We present a study of the high-temperature superconductor material $Bi_2Sr_2CaCu_2O_{8+x}$ (Bi2212) using M-EELS to measure low-energy electron dynamics. In optimally doped Bi2212, we find the emergence of static, short-range charge order at low temperature. The full measurement of $\chi''(\mathbf{q},\omega)$ shows low-energy charge excitations, and resolving these excitations in momentum space, we see these excitations carry a similar structure to the charge order, suggesting that the static electronic order modulates the many-body interaction. We show that this observation is qualitatively consistent with features observed in the single particle spectral function by ARPES, namely the nodal dispersion anomaly, or "kink". We performed a one-loop self-energy calculation to compute the dispersion and showed the interactions measured by M-EELS recovers the kink feature. This study leverages all three CES institutions, with Bi2212 crystals grown at Brookhaven National Lab, the M-EELS measurements acquired at University of Illinois, and the self-energy calculation performed at Argonne National Lab. Through this work, M-EELS provides insight into collective dynamics that drive high-temperature superconductivity and is a promising technique to advance our understanding of the high-T_c problem.



POSTDOCTORAL RESEARCHER FINALISTS

ULTRAFAST SYNTHESIS METAL-ORGANIC FRAMEWORKS CRITICAL FOR ENERGY-EFFICIENT CO_2 CAPTURE

[CGS] L. Maserati[1], S. M. Meckler[1,2] , C. Li[1,3], J. R. Long[2,4] and B. A. Helms[1]
[1]*The Molecular Foundry, Lawrence Berkeley National Laboratory;* [2]*Department of Chemistry, University of California, Berkeley;* [3]*Department of Chemical Engineering, University of California, Berkeley;* [4]*Materials Sciences Division, Lawrence Berkeley National Laboratory*

Metal-organic frameworks (MOFs) are microporous crystalline solids constructed from metal ions or clusters, which are covalently linked by organic ligands[1]. The tunability of their composition, architecture and properties has revolutionized the way we approach carbon capture and storage at CO_2-emitting power plants[2,3]. M_2(dobpdc) MOFs—and in particular their diamine-modified derivatives—have shown exceptional promise for energy-efficient CO_2 capture[4]. However, today's multi-hour synthetic procedures prevent their expedient and scalable production, which limits our ability to validate these materials in pilot-scale prototypes.

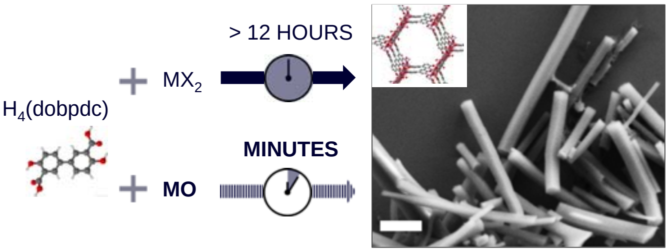


Fig. 3 M_2(dobpdc) synthesis concept and realization.

To address this challenge, we developed an exceptionally rapid synthesis of high quality M_2(dobpdc) where (dobpdc = 4,4′-dioxido-3,3′-biphenyldicarboxylate) that co-opts conventional divalent metal salts in favor of divalent metal oxides: MO = MgO, MnO, CoO, NiO, or ZnO. Our (pseudo)halide-free route avoids the generation of acidic by-products otherwise inherent to conventional M_2(dobpdc) syntheses[5]; as a result, the reaction time needed decreases significantly — in some cases, by several orders of magnitude (Fig. 1). We show that M_2(dobpdc) formation proceeds via a dissolution-precipitation mechanism. Through our analysis of MO precursor morphology, surface area, and composition-dependent etch rate, we determined that MO dissolution is rate-limiting. Notably, then, scaling the dimensions of the MO precursor to nanoscopic dimensions allows these MOFs to be prepared in high quality in mere minutes without residual MO. As a penultimate demonstration, we synthesized Zn_2(dobpdc) MOFs from 7 nm ligand-stripped[6] ZnO colloidal nanocrystals (NCs) in less than 1 minute. Our discovery highlights the role for basic science to guide methods of production of critical materials for energy-efficient CO_2 capture.

[1] Rowsell, J. L. C. & Yaghi, O. M. Metal–organic frameworks: a new class of porous materials. *Met.-Org. Open Framew.* **73,** 3–14 (2004).
[2] Boot-Handford, M. E. *et al.* Carbon capture and storage update. *Energy Environ. Sci.* **7,** 130–189 (2014).

ACID GAS INTERACTION WITH OXIDE NANOSHAPES WITH WELL-DEFINED SURFACE FACETS

[UNCAGE-ME] Uma Tumuluri[1], Meijun Li[1], Brandon Cook[2], William Mounfield[3], Joshua D. Howe[3], Bobby Sumpter[2], Krista S. Walton[3], David S. Sholl[3], Sheng Dai[1], Zili Wu[1,2]
[1]Chemical Science Division, Oak Ridge National Laboratories; [2]Center for Nanophase Material Science, Oak Ridge National Laboratories; [3]School of Chemical & Biomolecular Engineering, Georgia Institute of Technology

Acid gases such as CO_2, SO_2, NO_x are ubiquitous in the energy applications. Nanoshaped oxides such as CeO_2, TiO_2 are widely used as adsorbents and catalysts in the energy applications. Prolonged interaction with the corrosive acid gases affects the surface and bulk properties of both metal catalysts and oxide supports. Fundamental understanding on how the acid gases interact with the catalysts and the effect of the surface structure, defects and dopants on the acid gas interaction is very important for designing more stable catalysts/adsorbents. To gain a fundamental understanding of how CeO_2 and TiO_2 are affected by the acidic CO_2/SO_2, we investigated the effect of the surface structure of CeO_2/TiO_2 on the nature and the strength of adsorbed CO_2 and adsorbed SO_x using in situ IR spectroscopic and mass spectrometric techniques. CeO_2 nanoparticles with different morphologies: rods, cubes, and octahedra and metal organic framework (MOF)-derived CeO_2 were used to represent different CeO_2 surfaces. TiO_2 nanoparticles with different morphologies: rods, disks, and octahedra and carbide-derived TiO_2 were used to represent different TiO_2 surfaces. IR spectroscopic studies indicate that SO_2 adsorbs in the form of surface and bulk sulfite/sulfates on CeO_2 and TiO_2 nanoparticles, and CO_2 adsorbs in the form of carbonates (monodentate, bidentate and bridged). The degree of the formation of adsorbed species depends on the shape of the CeO_2 and TiO_2 nanoparticles. The IR results were well substantiated by theoretical calculations of the structures and adsorption strength of the CO_2/SO_x species on intact and oxygen-vacancy involved CeO_2/ TiO_2 nanoparticles.

STRUCTURAL STUDIES OF PLANT CELLULOSE SYNTHASE SUPPORT 18 SYNTHASES IN THE CELLULOSE SYNTHESIS COMPLEX

[CLSF] Venu Gopal Vandavasi[1], B. Tracy Nixon[2], Daniel K. Putnam[3], Katayoun Mansouri[4], Jung-Goo Lee[4], Abhishek Singh[4], Juan Du[2], Eric M. Roberts[5], Alison W. Roberts[6], Erin Slabaugh[4], Jonathan K. Davis[4], Qiu Zhang[1], Loukas Petridis[1], William T. Heller[1], Udaya Kalluri[1], Leighton Coates[1], Paul Langan[1], Jeremy C. Smith[1], Jens Meiler[3], Yaroslava G. Yingling[4], Candace H. Haigler[4] Hugh O'Neill[1,7]

[1]Oak Ridge National Laboratory; [2]Pennsylvania State University; [3]Vanderbilt University; [4]North Carolina State University; [5]Rhode Island College; [6]University of Rhode Island; [7]University of Tennessee

Cellulose is the most important structural component of plant cell walls and constitutes the Earth's largest store of biorenewable material for liquid biofuel production for the transportation sector of the economy, yet the mechanism of its synthesis by plants is poorly understood. The plant cellulose synthesis complex (CSC), also called a 'rosette' because of its hexameric appearance in electron microscope images, is a large multi-subunit transmembrane protein complex responsible for synthesis of cellulose chains and their assembly into microfibrils. The number of cellulose synthase (CESA) proteins in the CSC and the number of cellulose chains in a microfibril have been debated for years. This work reports analysis of CSCs obtained using refined methods in freeze facture transmission microscopy (FF-TEM) and structural studies of a recombinant cytosolic domain of plant CESA in solution. Together, these studies provide new insights into the structure and oligomeric state of CESAs and the probable number of cellulose chains in the microfibril. Class averaging of the FF-TEM images of individual lobes in the CSC combined with computational modeling of the transmembrane helical (TMH) region of CESA revealed each lobe of the CSC likely contains three CESAs. Analysis of the individual lobes in the FF-TEM images indicates that the lobe-lobe interactions are relatively weak suggesting the forces that hold the CSC together must be due to protein-protein interactions in the cytosolic portion of CESA and/or glucan chain interactions near the plasma membrane surface. Small-angle neutron and X-ray scattering were used to study the solution structure of the cytosolic domain of Arabidopsis CESA1 (CESAcatD). *Ab initio* models for CESAcatD derived from the SANS and SAXS data provide the first experimental evidence to support the self-assembly of CESAcatD monomers into stable homotrimer complexes. By combining small-angle scattering data with computational approaches, possible configurations for the arrangement of CESAcatD monomers in the homotrimer were obtained. Several candidate trimers were identified with monomers oriented such that that newly synthesized cellulose chains project towards the cell membrane. In these models, the class specific region is found at the periphery of the complex and the plant-conserved region forms the base of the trimer. Comparison of the FF-TEM images with the sizes of a TMH trimer and a CESACatD trimer provides compelling evidence that each lobe of a CSC contains three CESAs. The combined data from the two studies refutes the long-standing model of 36 CESAs within the rosette CSC and strongly supports the 'hexamer of trimers' model for rosette CSC that synthesizes an 18-chain cellulose microfibril as the fundamental product of cellulose synthesis in plants.

DYNAMIC EVOLUTION OF NANOPOROUS GOLD CATALYSTS DURING ACTIVATION AND SELECTIVE OXIDATION REACTIONS

[IMASC] Branko Zugic[1], Lucun Wang[1], Michelle L. Personick[1], Matthew Montemore[2], Christian Heine[3], Luan Nguyen[4], Nare Janvelyan[1], Dmitri Zakharov[5], Eric Stach[5], Miquel Salmeron[3], Monika M. Biener[6], Juergen Biener[6], Franklin (Feng) Tao[4], Efthimios Kaxiras[2], Robert J. Madix[2], Cynthia M. Friend[1, 2]

[1]Department of Chemistry and Chemical Biology, Harvard University; [2]School of Engineering and Applied Sciences, Harvard University; [3]Materials Science Division, Lawrence Berkeley National Laboratory; [4]Department of Chemical and Petroleum Engineering and Department of Chemistry, University of Kansas; [5]Center for Functional Nanomaterials, Brookhaven National Laboratory; [6]Nanoscale Synthesis and Characterization Laboratory, Lawrence Livermore National Laboratory

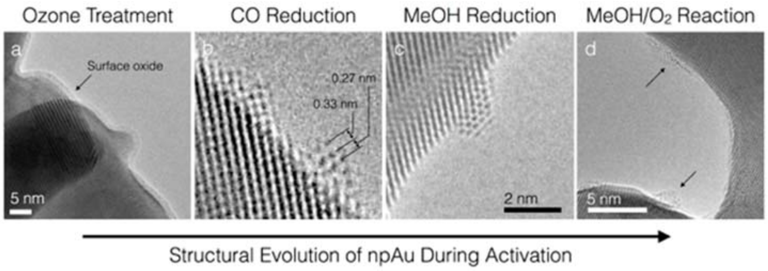


Figure 1. E-TEM study showing the structural rearrangements of the npAu surface after (a) ozone treatment (activation) (b) reduction by CO, showing removal of oxide and presence of defects (c) further reduction by MeOH, resulting in crystallization and (d) methanol oxidation reaction conditions, showing the fully evolved catalyst structure with regions of 'activity'.

Bimetallic catalysts are critical to the development of tunable material properties in order to address energy inefficiencies in catalytic processes. The dynamic nature of these materials has often been overlooked in their design. Nanoporous gold (npAu) is an unsupported metallic Au alloy with dilute Ag content. It requires activation with ozone in order to selectively catalyze the O-assisted coupling of methanol and other alcohols. We have shown that treatment of npAu by ozone at 150 °C followed by exposure to a methanol-oxygen mixture results in highly active and stable catalysts.[1] To understand the structural evolution and catalytic activity after ozone treatment, we have used a combination of reactor studies, theoretical calculations, atmospheric pressure X-ray photoelectron spectroscopy (AP-XPS), and electron microscopy (including environmental-TEM). The results show that dynamic structural changes take place at the npAu surface at different stages of the activation process as shown in Figure 1.[2] The ozone treatment causes near-complete oxidation of the npAu surface that results in amorphous layers of silver/gold oxides. This oxide layer gives rise to non-selective products (i.e. combustion). However, the 'oxidic' oxygen can be removed by CO titration, leading to metastable structures that are reactive selectively to methanol. These quasi-ordered structures appear to be responsible for the selective oxidation activity of npAu and are predicted by DFT studies. The results represent the potential of correlated *in-situ*/DFT studies and highlight their ability to improve our understanding of the dynamics of bimetallic catalysts.

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[2] Zugic, B.; Personick, M. L.; Janvelyan, N.; Wang, L.-C.; Zakharov, D.; Stach, E. A.; Madix, R. J.; Friend, C. M. *In Preparation.*

LIST OF EFRC ACRONYMS

Ordered by Acronym

[ANSER] Argonne-Northwestern Solar Energy Research Center
Michael Wasielewski, Northwestern University

[BETCy] Center for Biological Electron Transfer and Catalysis
John Peters, Montana State University

[C3Bio] Center for Direct Catalytic Conversion of Biomass to Biofuels
Maureen McCann; Purdue University

[CASP] Center for Advanced Solar Photophysics
Victor Klimov, Los Alamos National Laboratory

[CBES] Center for Bio-Inspired Energy Science
Samuel Stupp, Northwestern University

[CCDM] Center for the Computational Design of Functional Layered Materials
John Perdew, Temple University

[CCEI] Catalysis Center for Energy Innovation
Dionisios Vlachos, University of Delaware

[CE] Center for Excitonics
Marc Baldo, Massachusetts Institute of Technology

[CEES] Center for Electrochemical Energy Science
Paul Fenter, Argonne National Laboratory

[CES] Center for Emergent Superconductivity
Peter Johnson, Brookhaven National Laboratory

[CFSES] Center for Frontiers of Subsurface Energy Security
Larry Lake, University of Texas at Austin

[CGS] Center for Gas Separations Relevant to Clean Energy Technologies
Jeffrey Long, University of California, Berkeley

[CLSF] Center for Lignocellulose Structure and Formation
Daniel Cosgrove, Pennsylvania State University

[CME] Center for Molecular Electrocatalysis
R. Morris Bullock, Pacific Northwest National Laboratory

[CNGMD] Center for Next Generation of Materials by Design: Incorporating Metastability
William Tumas, National Renewable Energy Laboratory

[EDDE] Energy Dissipation to Defect Evolution
Yanwen Zhang, Oak Ridge National Laboratory

[EFree] Energy Frontier Research in Extreme Environments
Russell Hemley, Carnegie Institution of Washington

[FIRST] Fluid Interface Reactions, Structures and Transport Center
David Wesolowski, Oak Ridge National Laboratory

[GSCO2] Center for Geologic Storage of CO_2
Scott M. Frailey, University of Illinois at Urbana-Champaign

[ICDC] Inorganometallic Catalyst Design Center
Laura Gagliardi, University of Minnesota

[IMASC] Integrated Mesoscale Architectures for Sustainable Catalysis
Cynthia Friend, Harvard University

[LMI] Light-Material Interactions in Energy Conversion
Ralph Nuzzo, California Institute of Technology

[m2M] Center for Mesoscale Transport Properties
Esther Takeuchi, Stony Brook University

[MSA] Materials Science of Actinides
Peter Burns, University of Notre Dame

[NCGC] Center for Nanoscale Controls on Geologic CO_2
Donald DePaolo, Lawrence Berkeley National Laboratory

[NECCES] NorthEast Center for Chemical Energy Storage
M. Stanley Whittingham, Binghamton University

[NEES] Nanostructures for Electrical Energy Storage
Gary Rubloff, University of Maryland

[PARC] Photosynthetic Antenna Research Center
Robert Blankenship, Washington University in St. Louis

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

[SHINES] Spins and Heat in Nanoscale Electronic Systems
Jing Shi, University of California, Riverside

[UNC] Center for Solar Fuels
Thomas Meyer, University of North Carolina

[UNCAGE-ME] Center for Understanding and Control of Acid Gas-induced Evolution of Materials for Energy
Krista Walton, Georgia Institute of Technology