Leaders in Energy and the Environment Focus Topic
Room On Demand - Session LD-Contributed On Demand

Leaders in Energy and the Environment Contributed On Demand Session

LD-Contributed On Demand-1 Work Function Reduction of Carbon Nanospikes and the Effects of Contaminants by XPS and UPS, ***Arthur Baddorf**, D. Hensley,* Oak Ridge National Laboratory*; A. Rondinone,* Los Alamos National Laboratory

Carbon nanospikes show excellent energy and selectivity for electrochemical conversion of CO_2 to ethanol and N_2 to NH_3. Transmission electron microscopy (TEM) images reveal that these nanospikes are 50- 80 nm in height and terminated with a sharp tip of radius ~1 nm. It has been proposed that catalytic activity follows from an enhanced electric field from the sharp spike topography. We have tested this hypothesis through measurements of the absolute work function using ultraviolet photoemission spectroscopy (UPS). As samples were characterized after transfer through air, surface cleanliness was monitored with x-ray photoelectron spectroscopy (XPS). Annealing as-grown samples above 275 °C produces a clean surface which has a 4.13 eV work function, a half volt lower than that of flat graphite. This reduction supports the idea that a strong electric field is generated by the nanospike topography.

Contamination of the spiked surface raises the work function above that of the clean nanospikes. Work function values after exposure are increased to 4.19 eV for hydrocarbons, 4.30 for air, 4.42 for water, and 4.48 for oxygen. Blunting the spikes, by exposure to an oxygen plasma, argon sputtering, or annealing to 800 °C results in a work function close to that of flat graphite, 4.62 eV. An unusual double onset in the UPS secondary electron intensity is observed from as-grown nanospike samples and is reproduced by absorbing hydrocarbons on clean nanospikes. This double onset has not been reported on metal surfaces and appears to be unique to carbon substrates. The energy difference between the two onsets, about 0.4 eV is close to that of a typical C-H stretch in hydrocarbons suggesting the lower energy onset may originate in inelastic scattering of photoelectrons.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility

LD-Contributed On Demand-4 Electrochemical Performance of $CaFe_2O_4$ Synthesized at Multiple Fuel-to-Oxidizer Ratios, ***Jacob Strimaitis**, S. Danquah, C. Denize, C. Bonner, S. Pradhan, M. Bahoura,* Norfolk State University

Porous $CaFe_2O_4$ (pCFO), a promising conversion-type anode material for next-generation lithium-ion batteries (LIB) and hybrid supercapacitors (HSC), is relatively easy to produce via solution combustion synthesis (SCS). However, despite evidence that the morphology, composition, and electrochemical performance of metal oxides can be enhanced by changing the fuel-to-oxidizer ratio during SCS, such treatment has yet been applied to pCFO. In this study it is demonstrated that increasing the ratio across a “moderately fuel-lean” to “moderately fuel-rich” range increases the porosity, inter-particle conglomeration, and specific capacity of pCFO, further cementing the importance of stoichiometric considerations in SCS. Future implications of extending the range of the ratio and optimizing calcination temperature and time in order to reach the theoretical capacity target are also discussed.

LD-Contributed On Demand-7 Modern Devices from Old Materials - Selenium and Selenium-Tellurium Alloys Thin Film Solar Cells, ***Ido Hadar**,* The Hebrew University of Jerusalem, Israel*; T. Song, W. Ke, X. Hu, Z. Luo, V. P. Dravid, M. Kanatzidis,* Northwestern University

The photovoltaic properties of selenium were discovered about 150 years, and shortly afterward, selenium was utilized to fabricate the first 'thin-film' solar cell. This discovery led to modern research of semiconductors and development of related technologies. Selenium was implemented in many of these devices and applications. Following the rise of alternative semiconductors, and specifically silicon, the usage of selenium slowly declined. In recent years, the search for simple and scalable photovoltaic materials has revived the research of selenium as an elemental semiconductor that may be implemented as a possible absorber for extremely low-cost and highly scalable solar cells. Selenium has few desirable properties for these devices such as high absorption coefficient, intrinsic environmental stability, and low-temperature fabrication (below 200°C). Herein we study the main parameters that define the quality and efficiency of selenium-based thin-film solar cells, fabricated by vacuum thermal evaporation, and optimize them using modern tools and approach. We found that careful annealing of the selenium film, very close to its melting temperature, is essential to obtain high-quality crystalline films. Moreover, the anisotropic structure of selenium, composed of 1D chains, suggests that alignment of the crystals in the thin film may improve the device properties, and we study the means to control the film orientation. Finally, we indicate the importance of light illumination (and excitation) of the film during the annealing process, enhancing and improving the film's crystallization.

Following these results, we study how the selenium bandgap (1.7 eV), can be tuned to the optimal value for photovoltaic absorber (1.2-1.4 eV), by alloying selenium with the isomorphic low bandgap semiconductor tellurium. Selenium-tellurium alloys exhibit a strong non-linear shift of the conduction band minimum energy, leading to a non-linear decrease of the bandgap. Consequently, the desired bandgap energy can be obtained by alloying a relatively small amount of tellurium (~10%). Thin-film solar cells based on the selenium-tellurium alloy indeed show improved current density and spectral response due to the optimized bandgap. The overall efficiency of the selenium-tellurium devices is still lower than the pure selenium devices, due to lower voltage and fill-factor. We indicate the leading causes for the lower properties and suggest how to resolve them and improve the device efficiency.

(1) Hadar, I.; Song, T. Bin; Ke, W.; Kanatzidis, M. G. Modern Processing and Insights on Selenium Solar Cells: The World's First Photovoltaic Device. Adv. Energy Mater. **2019**.

(2) Hadar, I.; Hu, X.; Luo, Z.-Z.; Dravid, V. P.; Kanatzidis, M. G. Nonlinear Band Gap Tunability in Selenium–Tellurium Alloys and Its Utilization in Solar Cells. ACS Energy Lett. **2019**, 4 (9), 2137–2143.

LD-Contributed On Demand-10 A Combined DRIFTS and Theoretical Study of the Mechanisms of Aldol Condensation of Acetaldehyde on CeO_2(111), ***Suman Bhasker-Ranganath**, M. Rahman, C. Zhao,* Louisiana State University*; F. Calaza,* Instituto de Desarrollo Tecnoloǵico para la Industria Química , Argentina*; Z. Wu,* Oak Ridge National Laboratory*; Y. Xu,* Louisiana State University

Aldol condensation creates C-C bonds between organic oxygenates, providing a useful pathway for upgrading of biomass-derived feedstock to fuels and higher value chemicals. To develop a better understanding of this reaction and factors that limit activity and selectivity on ceria, we have explored the reaction pathways for self-condensation of acetaldehyde (AcH) to crotonaldehyde (CrH) on ceria nano-octahedra using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and modeling based on DFT calculations.

As opposed to a lack of C-C coupling activity in UHV,[1] we find that CrH forms readily on ceria nano-octahedra at ambient temperature under a flow of AcH. All major peaks detected in DRIFTS are assigned conclusively by comparison with simulated IR spectra to either AcH*, *trans*-CrH*, or a stable intermediate state, as adsorbed on CeO_2(111). The reaction on stoichiometric sites proceeds through enolization of AcH and C-C coupling between the enolate and molecular AcH. The C-C coupled intermediate transforms into 3-hydroxylbutanal (3HBtL), which further enolizes and dehydroxylates to form CrH. A slightly less stable *cis* isomer of CrH* forms via the same reaction pathway with different molecular orientations in C-C coupling, but the *trans* isomer is more stable and is estimated to dominate in coverage. The reaction, when occurring on a point surface oxygen vacancy (V_O), leads to a build-up of the enolate of 3HBtL/V_O, with a 1620 cm^{-1} peak in the DRIFTS spectra that is assigned to νC=C mode of this intermediate. Desorption of CrH from V_O is much more hindered than from stoichiometric sites, so V_O is not an active site at ambient temperature.[2]

Analysis of the reaction kinetics suggests that, the desorption-limited reaction rate should be zero-order in AcH partial pressure if the surface is mostly occupied, or second-order if the reaction is at low conversion. For this and similar reactions, therefore, enhancing facile product desorption would be key to having a workable catalyst based on ceria or similar oxides.

(1) Chen, T. -L.; Mullins, D. R., *J. Phys. Chem. C.*115 **(2011)** 3385-3392; Zhao, C. et al., *J. Phys. Chem. C.*123 **(2019)** 8273-8286.

(2) Bhasker-Ranganath, S. et al., *ACS Catal.* (**2021**).

LD-Contributed On Demand-13 Atomic-Scale Insights Into the Workings of Pt-Based Copper Oxide Single-Atom Catalysts*, **Audrey Dannar**, A. Schilling, G. Giannakakis, A. Therrien, C. Sykes,* Tufts University

Single-atom catalysts are often comprised of isolated metal atoms anchored on oxide supports and have recently gained considerable attention for their improvements in selectivity and reactivity for important industrial reactions such as preferential oxidation of CO. We have previously shown that single Pt atoms on an atomically thin copper oxide film grown on Cu(111) are able to perform low temperature CO oxidation without sintering, a common deactivation mechanism of single atom catalysts. Using a combination of scanning tunneling microscopy, infrared and x-ray photoelectron spectroscopy, and temperature programmed desorption experiments we elucidated the atomic-scale surface structure of these model catalysts and related that structure to catalytic function. We found that Pt atoms have a preferred binding site on the oxide surface and preferentially activate CO but not H_2. These results were then used to design a nanoparticle catalyst analog which functions under industrially relevant preferential oxidation of CO in H_2 (CO-PROX) conditions. Moving beyond this initial work which made use of a thin film oxide, we are now in the process of characterizing the 111 facet of a bulk Cu_2O single-crystal. This will provide a useful model catalyst surface as it better mimics the Cu_2O particles present in high surface area catalysts. Taken together, our thin-film and bulk copper oxide surfaces with isolated Pt atoms further the atomic-scale understanding of single-atom catalysts which should aid in the rational design of next-generation catalysts.

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Leaders in Energy and the Environment Invited On Demand Session

LD-Invited On Demand-1 Atomic-Scale Imaging of Optically-Active Nanoscale Systems*, **Jeffrey R. Guest**,* Argonne National Laboratory **INVITED**

Optical interactions and photophysical processes hinge on structure and the local environment in nanoscale systems, it is critically important to develop experimental approaches which can characterize these optical properties and correlate them with atomic-scale morphology and electronic structure. Over the past three decades, ultra-high vacuum (UHV) scanning tunneling microscopy/spectroscopy (STM/STS) and associated surface preparation techniques have demonstrated atomic-scale control over nanoscale structures.In parallel, single-particle laser spectroscopy has elucidated photophysics, quantum coherence, and optical properties with ultrahigh spectral resolution at the single quantum absorber and emitter level.

In this talk, I will focus on our efforts to extend these studies to the atomic scale on surfaces by combining UHV STM and single particle laser spectroscopy. I will discuss our work exploring the structural, electronic, and transport properties of donor-acceptor molecular heterojunctions (HJs) self-assembled from C60 and pentacene as a potential platform for exploring photophysics at the molecular scale. We have resolved a surprising structure and charge transfer in in-plane molecular HJs [1], and demonstrated extremely strong (and spatially dependent) current rectification in transport for a stacked molecular HJ at the monolayer level [2].I will discuss recent STM/STS measurements on defects in bilayer WSe_2, which may be related to the single-photon emitting defects observed in laser spectroscopy experiments, revealing the local electronic structure and demonstrate the ability to control the charge state of these defects [3]. Time permitting, I will discuss UHV STM measurements on Cu2O (111) and (110) surfaces and our efforts to understand their physical and electronic structure in light of their photocatalytic activity [4].

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1. J. A. Smerdon *et al.,* ACS Nano 7, 3086 (2013).
2. J. A. Smerdon *et al.,* Nano Letters 16, 2603 (2016).
3. R. Zhang *et al*., J. Phys. Chem. C, *in press.*
4. R. Zhang *et al.,* Phys. Chem. Chem. Phys*,* 20, 27456 (2018).

LD-Invited On Demand-7 Probing Molecule-Substrate Interactions at Angstrom Scale by Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy*, **Nan Jiang**,* University of Illinois at Chicago **INVITED**

To demonstrate the effect of local environments on complex chemical systems, we designed a series of tip-enhanced Raman spectroscopy (TERS) experiments to study molecule-substrate interactions at angstrom scale. We chose subphthalocyanine molecules deposited on a Ag(100) surface as an example of weak interactions between the molecules and the substrate. We were able to ascertain subtle vibrational modes which showed an excellent agreement between experimental spectra and simulated Raman spectra of gas phase molecules. In another case, a strong interaction with the surroundings leads to symmetry breaking, allowing us to separately detect intermolecular interactions such as electrostatic attractions by using TERS. In combination with theory, we revealed the lifting of vibrational degeneracy inside a molecular self-assembly due to strong lateral intermolecular interactions. To address the inability of scanning tunneling microscopy (STM) to study the configurations of adsorbed non-planar molecules on surfaces, we used TERS to unambiguously determine the tilt or orientation of molecules on a surface. Due to the selection rules for TERS, vibrational modes that are perpendicular to the surface and parallel to the tip and enhanced EM field are the most strongly enhanced. Since TERS spectra rely upon molecular orientation, we identified multiple orientations of rubrene on a Ag(100) surface. The sensitivity of TERS to molecular orientation combined with our 5.5 angstrom spatial resolution demonstrates a unique analytical technique for similar non-planar molecules. We also reported the first demonstration of STM-TERS towards the study of isomeric nonplanar adsorbates on three different well-defined substrates, Ag(100), Cu(100) and Au(100). We demonstrated the effects of surface interactions on the vibrational modes of molecules, indicating that the substrate is an intriguing parameter to manipulate the self-assembly and configurations of ad-molecules. Together, our work allows the definitive identification of multiple orientations of individual molecules and their dependence upon highly localized chemical environments.

LD-Invited On Demand-13 HAXPES for Device Applications: From the Surface into the Bulk*, **Anna Regoutz**,* University College London, UK **INVITED**

X-ray photoelectron spectroscopy (XPS) is based on the photoelectric effect discovered and described by Planck, Einstein and Millikan, and has its beginnings in the ground breaking work of Kai Siegbahn, who received the Nobel Prize in Physics in 1981 for the development of the technique. XPS can non-destructively probe the chemical composition, local chemical environments, and electronic structure of matter, and since its invention it has been applied to a vast range of materials, including solids, liquids, and gases. The most common variety of XPS uses soft X-ray sources, e.g. Al Kα at 1.5 keV, giving extremely surface sensitive results probing only the first few nanometres of a sample's surface.

Hard X-ray excitation sources with energies of up to 10 keV extend the probing capabilities of XPS beyond the outermost surface of materials by enabling photoelectrons from much deeper regions to be detected. Hard X-ray photoelectron spectroscopy (HAXPES) delivers much greater probing depths of tens of nanometres enabling the characterisation of buried layers and interfaces in structured materials, e.g. thin film stacks and core-shell nanoparticles, as well as bulk characteristics of homogeneous samples. Like XPS, HAXPES enables the study of both chemical states and electronic structure. Over the last decade the development of advanced beamlines at synchrotrons in parallel with the advent of laboratory-based spectrometers has opened up HAXPES for a much wider range of materials and applications.

This talk will give an introduction to the general capabilities of HAXPES. It will provide an overview of the additional challenges and opportunities that HAXPES presents and will cover recent developments and results of this emerging technique.

LD-Invited On Demand-19 Nanoparticle Size, Shape, Composition and Support Effects in the Hydrogenation of Carbon Dioxide*, **Beatriz Roldan Cuenya**,* Fritz-Haber Institute of the Max Planck Society, Germany **INVITED**

The selective hydrogenation of CO_2 to methanol and high-order hydrocarbons is a promising process for establishing a methanol economy and recycling CO_2. Although for the methanol synthesis there is a well-established industrial process based on a $Cu/ZnO/Al_2O_3$ catalyst, open questions still remain relative to the reaction mechanism and the active phases involved. The same applies to the "modified" Fischer-Tropsch process commonly catalyzed by Fe-based materials where the oxidation state of the active catalyst and the possible formation of carbide species is debated.

Since these reactions are catalyzed by nanostructured materials, tailoring their chemical reactivity at the atomic level will be the challenge to address. In order to accomplish this, we must first obtain a fundamental understanding of the structural and chemical properties of complex nanoscale systems. In addition, the dynamic nature of the nanoparticle (NP) catalysts and their response to the environment must be taken into consideration. To address the complexity of real-world nanocatalysts, a synergistic approach taking advantage of a variety of cutting-edge experimental methods (AFM, TEM, TPD, NAP-XPS, XAFS, MS/GC) has been undertaken.

Catalytically active size- and shape-controlled NPs (Fe, Cu, Cu-Zn, Cu-Ni, Cu-Ga) will be synthesized via colloidal chemistry and compared to model NP systems synthesized via physical vapor deposition. Structure/composition-reactivity correlations *in situ* and under realistic *operando* reaction conditions, i.e., at high pressure will be investigated. In particular, the role of the NP size, shape (spherical vs cubic NPs), surface composition (alloy, core-shell) and support (ZnO, Al_2O_3, ZnOAl, SiO_2, ZrO_2) in the activity and selectivity will be addressed. Our results are expected to provide the required fundamental understanding that might lead to new routes for the reutilization of CO_2 through its direct and selective conversion into valuable chemicals such as methanol or high order hydrocarbons.

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