

Friday Morning, November 2, 2012

Energy Frontiers Focus Topic

Room: 15 - Session EN+SS-FrM

Photocatalysis and Solar Fuels

Moderator: N.G. Petrik, Pacific Northwest National Laboratory

8:20am EN+SS-FrM1 **Atomic Layer Deposition for Electronic Band Engineering of Silicon Photoelectrochemical Cells**, *B. Kalanyan, M.D. Losego, D.H. Kim, G.N. Parsons*, North Carolina State University

Nanostructured semiconductor materials are generating considerable interest for application in photoelectrochemical cells (PEC) for solar water splitting. A key challenge is improving the long-term chemical and operational stability of semiconductor electrodes. Our research in PEC devices focuses on utilizing atomic layer deposition (ALD) as a means to engineer the semiconductor-liquid interface of photoelectrodes. ALD modification can both impart chemical stability and tune the electronic band structure at the semiconductor's surface. P-type silicon photocathodes are a model PEC system capable of high photocurrents (>10 mA/cm²) in aqueous electrolytes under AM 1.5 illumination. Here we will detail our efforts to improve the reproducibility of silicon photocathode fabrication and to use TiO₂ ALD coatings for band engineering that permits planar catalyst integration.

This talk will discuss silicon photocathodes fabricated from p-type Si (100) wafers with ~ 1 cm² functional area. Electrodes were tested in a three-electrode electrochemical cell containing sulfuric acid electrolyte (0.5M, pH ~ 0), a Pt mesh (>5 cm²) counter electrode, and a Ag/AgCl reference electrode. To ensure similar dopant profiles, experiments were run using a range of silicon samples from the same wafer. We will first discuss the effects of varying the processing schemes for forming an ohmic back contact. We find a large and distinct effect on both the photocurrent saturation value and the photocurrent onset potential with the size and composition of this back contact. Through contact optimization, series resistance of the back contact can be reduced by 5x, as measured by impedance spectroscopy.

The second portion of our talk will describe our results using ALD TiO₂ thin films to engineer the electronic band structure at the photocathode/electrolyte interface. Deposition of a coalesced Pt thin film catalyst layer directly on p-type silicon is well known to form an Ohmic contact that pins the silicon's Fermi level in a nearly flat band state. Without the internal bias caused by surface carrier depletion, photoelectrode activity is eliminated. However, by inserting an interfacial TiO₂ layer with sub-nanometer thickness control, a p-n junction can be formed which generates the necessary electric field for photoelectrode operation. Here, we will demonstrate how uniform ALD layers are capable of providing the necessary electronic band engineering to form completely planar p-Si/TiO₂/Pt structures with photocurrents exceeding 10 mA/cm² with no applied bias.

8:40am EN+SS-FrM2 **Photochemical Hole Scavenging Reactions of Methanol on TiO₂: Identification of Active Species and Water Coadsorption Study**, *M. Shen, M.A. Henderson*, Pacific Northwest National Laboratory

Molecular and dissociative forms of adsorbed methanol were prepared on the rutile TiO₂(110) surface to study their relative photocatalytic activity for hole-mediated oxidation. Molecular methanol is the dominant surface species on the vacuum-annealed TiO₂(110) surface in ultrahigh vacuum (UHV). Coadsorption of methanol with oxygen results in $\sim 20\%$ of the adsorbed methanol decomposing to methoxy and OH. Subsequent heating of the surface to 350 K leaves a surface with only adsorbed methoxy groups. Using temperature-programmed desorption, we show that adsorbed methoxy is at least an order of magnitude more reactive than molecularly adsorbed methanol for hole-mediated photooxidation. Methoxy photodecomposes through cleavage of a C-H bond forming adsorbed formaldehyde and a surface OH group. These results suggest that methoxy, and not molecular methanol, is the effective hole scavenger in photochemical reactions of methanol on TiO₂. Same reactions were also studied with water coadsorption.

9:00am EN+SS-FrM3 **Nanostructured Antimony Doped Tin Oxide Enhances Photoelectrochemical Water Splitting by Supported TiO₂**, *Q. Peng*, Duke University, *B. Kalanyan*, North Carolina State University, *M. Andrew, P. Hoertz*, Research Triangle Institute, *L. Alibabaei*, University of North Carolina at Chapel Hill, *J. Liu*, Duke University, *T.J. Meyer*, University of North Carolina at Chapel Hill, *G.N. Parsons*, North Carolina State University, *J.T. Glass*, Duke University

Photoelectrochemical (PEC) water splitting devices hold great promise for harvesting solar energy, however, existing electrodes suffer from either stability or efficiency limitations. Owing to its low production cost, environmental compatibility, and remarkable stability, TiO₂ has been widely investigated as a PEC electrode since 1972. However, the solar-to-fuel conversion efficiency of TiO₂ PEC electrodes is still much lower than the theoretical value. This is partially due to the dilemma of short minority carrier diffusion length and long optical absorption length, as well as the low electron mobility. Nanostructured conductive scaffolds show promise to solve this challenge by decoupling light absorption and charge carrier diffusion while enhancing conductivity. In this research, we synthesized TiO₂ PEC electrodes on a conductive scaffold comprised of antimony doped tin oxide particles (ATO-particle film). These structures, which are a cost effective alternative to semiconductor supported TiO₂ electrodes, yielded a photocurrent density of 0.58 mA/cm². This is approximately 3 \times the corresponding current density for planar TiO₂ PEC electrodes on FTO glass. Our results have shown that the porosity of ATO-particle film has limited the further efficiency improvement, which can be addressed by optimizing particle size, thickness, and assembly strategy for ATO-particle films. Owing to its transparency in a wide range of wavelengths, the ATO-particle scaffold also has great potential to boost the efficiency of devices using other narrow bandgap PEC materials, e. g. Fe₂O₃.

9:20am EN+SS-FrM4 **Plasmon-Mediated Charge Transfer in Au-TiO₂ Heterostructures for Visible Light Water-Splitting**, *J. DuChene, B. Sweeny*, University of Florida, *A. Johnston-Peck, D. Su*, Brookhaven National Laboratory, *W.D. Wei*, University of Florida

Solar water splitting to produce hydrogen represents a potential approach to satisfy the global energy demand in a sustainable manner. Recently it has been reported that the incorporation of plasmonic nanoparticles into semiconductor architectures offers a potential route to increase the efficiency of photoelectrochemical water splitting due to the unique optical properties of plasmonic nanomaterials. We investigated the energetics and dynamics of electron flow in Au-TiO₂ heterostructures following excitation of the Au nanoparticles surface plasmon resonance with visible light. Our results show that the incorporation of Au nanoparticles into wide band gap semiconductors has promise for use as visible light sensitizers. Moreover, we have studied the role of the hole scavenger methanol in the plasmon-mediated charge transfer process in order to ascertain the nature of possible thermodynamic or kinetic limitations involved in this process. These results demonstrate that the excited-state lifetime of these hot electrons in the TiO₂ conduction band is dramatically extended relative to direct band gap excitation within the semiconductor itself, suggesting a possible strategy for improving the efficiency of photocatalytic reactions.

9:40am EN+SS-FrM5 **Narrowing of Band Gap in 1D Arrays of TiO₂ Nanoparticles for Photocatalysis: Studies using X-ray Spectroscopies with In Situ Water Exposure and Heating**, *Y. Liu, J. Taing*, University of California Irvine, *C.C. Chen*, SLAC National Accelerator Lab, *A. Sorini*, Lawrence Livermore National Lab, *M.H. Cheng*, University of California Irvine, *H. Bluhm, Z. Liu*, Lawrence Berkeley National Lab, *T. Devereaux*, SLAC National Accelerator Lab, *J.C. Hemminger*, University of California Irvine

Titanium(IV) oxide (TiO₂) has a wide range of applications in energy science and acts as a stable support for photocatalysts and sensitizers. Utilizing ambient pressure synchrotron x-ray photoelectron and absorption spectroscopies, we explore the properties of TiO₂ thin films and ordered linear arrays of TiO₂ nanoparticles under *in situ* water vapor exposure and heating. Our nondestructive depth profiles (obtained by varying the photoelectron kinetic energy) of electronic and surface structures, combined with density-functional theory calculations, indicate an enhancement of the density of states (DOS) near the Fermi level due to surface Ti³⁺ and oxygen vacancies. Introducing water on the interface suppresses this DOS enhancement. The Ti L-edge and O K-edge absorption spectra, in combination with atomic multiplet calculations, provide information on crystal field effects and multiplet interactions, helping to determine the phases of the TiO₂ particles. Our *in situ* studies suggest that isolated TiO₂ nanoparticles may enhance solar absorption efficiency, and the TiO₂ band gap can be tuned reversibly under water exposure and heating.

10:00am **EN+SS-FrM6 A Theoretical Study of Carbon Dioxide Reduction on Catalysts**, *T. Liang, Y.-T. Cheng, S.R. Phillpot, S.B. Sinnott*, University of Florida

Catalytic reduction of carbon dioxide into fuels would provide an ideal storage medium for intermittent renewable energy sources. Copper and copper oxides electro-catalysts have been found to be capable of producing significant quantities of hydrocarbons or alcohols from CO₂ in aqueous solutions. Selectivity to methanol is speculated to be due to Cu(I) species in electrochemical systems; however, these pathways have not been experimentally verified. Here, the third-generation charge optimized many body (COMB3) potentials, which are proven to be successful to characterize different types of bonding in the heterogeneous systems, are employed to investigate the atomic scale mechanisms associated with catalytic reactions on Cu surfaces and clusters supported on metal oxide surfaces. In particular, the reaction free energies of selected CHO molecules on the Cu (211) surface are investigated and validated with density functional theory calculations. The electrochemical systems are simulated with room temperature, low-energy (5 or 10 eV) deposition of CO₂ or CO₂+H₂O on the Cu (211) surface and Cu cluster interface with the ZnO (101-1) surface. The results suggest that the higher incident energy and the presence of water molecules facilitate CO₂ dissociation. The charge state of the Cu cluster and the charge transfer process are predicted to play significant roles in the selectivity of the catalysts. In particular, the Cu(I) species at the Cu/ZnO interface are predicted to be preferable sites for CO₂ reduction and dissociation, which is consistent with experimental observations. This work was supported as part of the Center for Atomic Level Catalyst Design, 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-SC0001058.

10:20am **EN+SS-FrM7 Doping Effects on the Electronic Structure of Graphitic C₃N₄ Photocatalysts: Insights from First Principles**, *S. Zuluaga, S. Stolbov*, University of Central Florida

Band gap engineering and facilitating charge separation in the graphitic C₃N₄ semiconductors are promising means for improving the photocatalytic activity of these materials. A number of experiments suggest that doping of C₃N₄ is an efficient way to increase the rate of hydrogen production from water using this photocatalyst. In this work we apply a first principles computational approach to reveal the main factors controlling the S and P doping effects on the properties of C₃N₄. Our density-functional-theory-based calculations show that these dopants are bound to the edges of the triazine elements rather than substituting N or C. Valence charge density analysis provides detailed description of the charge transfer upon doping. We show, for example, that S does not work as an anion in these materials: it does not accept, but donates electronic charge to the C – N system. Using the GW method we calculate with high accuracy the electronic structure, including the band gap, of the pristine and doped C₃N₄. We show that sufficiently large S doping make the system a conductor. The obtained results shed light on how doping affect the catalytic properties of C₃N₄.

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