

Friday Morning, October 22, 2010

Energy Frontiers Topical Conference
Room: Mesilla - Session EN+SS-FrM

Photocatalysis and Solar Fuels

Moderator: S.-H. Lee, University of Colorado

8:20am **EN+SS-FrM1 Hybrid Metal-Semiconductor Nanomaterials for Electrochemical Hydrogen Generation, M.R. Dirmyer, E.P. Luther, A.K. Burrell, B.C. Tappan, A.H. Mueller, Los Alamos National Laboratory**

For the full utilization of intermittent alternative energy sources such as wind and solar energy, issues regarding energy storage must be addressed. An attractive solution is the production of a chemical fuel, allowing for both storage and transportation from so called "stranded" production sites. The electrochemical splitting of water to generate hydrogen allows for the production of such fuel, be it in a denser chemical form or H₂. Electrode materials for such an electrocatalytic process must have a high surface area, and be catalytically efficient and robust in order to be viable for such a process.

The research presented addresses the aforementioned challenges using two elegant, Los Alamos National Lab exclusive nanotechnologies: 1) combustion synthesis of conducting noble metal nanofoam scaffolding to serve as the cathode and 2) Polymer Assisted Deposition (PAD) of catalytically active films onto a conductive metal scaffold to functionalize the anode. The resulting foams have ultralow densities, controlled nanopore diameters, and rank with the highest surface area metals ever produced, making them ideal candidates for various catalytic applications. The deposition mechanism of PAD, as well as the high conductivity of the metal foam, enables the utilization of the entire interior surface of the foam for electrochemical reactions, exploiting the advantages of the thin film form of the coating while retaining the electrical advantages of a bulk metal electrode. Metallic copper foams have been coated with CIS-based thin-film absorber layers. These materials show photocurrent under illumination with 1.5 AM solar simulated light. Electrochemical water-splitting data will also be presented.

8:40am **EN+SS-FrM2 Surface Electronic Properties of Tantalum Oxynitride Perovskites, S. Balaz, S. Porter, P.M. Woodward, L.J. Brillson, The Ohio State University**

We used a complement of X-ray photoemission spectroscopy (XPS), depth-resolved cathodoluminescence spectroscopy (DRCLS), Kelvin Probe Force Microscopy (KPFM), and Atomic Force Microscopy (AFM) to measure the surface electronic properties of the tantalum oxynitride series ATaO₂N (A = Ca, Sr, Ba) and RTaON₂ (R = La, Pr), promising candidates for photocatalytic splitting of water under illumination by visible light. Besides creating perovskites with band gaps that straddle the redox potentials of water closely, a major challenge to conversion efficiency is the recombination of free carriers by trap states formed by lattice defects. We used DRCLS to measure the energies and densities of these recombination centers with respect to the bulk oxynitride energy bands and Fermi levels. Previously reported UV-VIS diffuse reflectance measurements indicate band gap absorption onsets at 2.4, 2.1, 1.8 [1], 2.0, and 2.0 eV [2] for CaTaO₂N, SrTaO₂N, BaTaO₂N, LaTaON₂ and PrTaON₂, respectively. DRCL spectra reveal both broad band-to-band transitions in the 2-5 eV range as well as intense and narrow sub-band gap peak features at 1.95, 1.70, 1.70 and 1.79 ± 0.01 eV for the same oxynitride sequence. The relatively constant DRCLS gap state energies indicate similar defects derived from the oxygen and nitrogen 2p orbitals comprising the valence band for all five compounds. By varying the incident beam energy, we probed the surface to the bulk with DRCLS, showing these peak energies nearly unchanged as a function of depth. However 0.1-0.2 eV shifts within the outer 10 nm suggest surface interactions that modify these localized states. The higher energy CL features reflect the slowly rising conduction band densities of states plus more pronounced O 2p-Ta 5d transitions calculated by density functional theory [1]. XPS valence band spectra show Fermi levels 0.5-2 eV above the valence bands, while KPFM work functions vary in the range 4.7 – 4.9 eV, indicating valence band maxima comparable to the 5.67 eV oxidation potential of water. Charging and potentials that vary laterally with nanoscale thickness can affect the XPS and KPFM values significantly but not DRCLS. The appearance of strong defect emissions at energies well within the band gap is indicative of strong recombination that can limit optical conversion efficiencies. Hence, these studies reveal the importance of O- and N-derived native point defects in limiting the efficiency of oxynitride photocatalysts.

[1] Y.-I. Kim, P. M. Woodward, K.Z. Baba-Kishi, and C.W. Tai *Chem. Mater.* 2004, **16**, 1267.

[2] S. Porter, Y.-I. Kim, P. Woodward, Am. Phys. Soc. March Meeting, March 15-19, 2010, abstract X27.00003.

9:00am **EN+SS-FrM3 Zinc-Gallium Oxynitrides as Visible-Light Photocatalysts: Band Gaps and Formation Energies, H. Schmidt, D.J. Doren, V.B.R. Boppa, R.F. Lobo, University of Delaware**

Solid solutions of GaN and ZnO have been shown to be a promising class of photocatalysts, capable of splitting water under visible-light irradiation. The structural and electronic properties of Ga_{1-x}Zn_xN_{1-x}O_x have been studied using density-functional theory with the Linear Augmented Plane Wave (LAPW) method at varying values of x. A GGA+U approach is used to better describe the semicore 3d states of Ga and Zn. These calculations show that there exists a p-d coupling between the N 2p and Zn 3d states, leading to a decreased band gap. The band gaps in the mixed metal oxynitrides are lower than either ZnO or GaN, thus allowing excitation by visible light. The trend in band gaps over the range of Zn concentrations (x) is consistent with experimental results. The expected band gap minimum is at a composition that is difficult to synthesize. Formation energies have been calculated to understand the limitations on synthesis of these materials. Several starting materials and synthesis environments have been studied in the formation energy calculations to determine how the thermodynamically preferred products depend on experimental conditions and whether high concentrations of zinc can be obtained in these materials.

9:20am **EN+SS-FrM4 Electronic Structure Analysis and Photocatalytic Properties of Novel Spinel Zinc Gallium Oxy-Nitride Semiconductors, B. Boppa, H. Schmidt, D.J. Doren, R.F. Lobo, University of Delaware**

A sol-gel precursor was used to synthesize zinc gallium oxy-nitrides with visible light band gaps. At low temperatures, novel spinel oxynitrides were produced with band gaps of 2.5 to 2.7eV, surface areas of 16 to 36 m²/g, and nitrogen content less than 1.5%. As the temperature was raised, these spinels get consumed to form wurzitic oxy-nitrides also with band gaps less than 3 eV but with surface areas of 4 to 6 m²/g. The reduction in the band gap for the spinel oxy-nitrides is associated with the incorporation of N2p orbitals in the valence band with corresponding changes in the anion position parameter. We established that the presence of a small fraction of gallium tetrahedral centers and anion vacancies might affect its unique electronic properties. The changes associated with the gallium coordination environment as the spinel zinc gallate precursor transforms to a spinel oxynitride at 550°C and further changes into a wurzite oxynitride at 850°C are studied through x-ray diffraction, ultraviolet-visible diffuse reflectance spectroscopy, neutron powder diffraction, x-ray absorption spectroscopy and other techniques. Electronic structure and formation energies of the spinel and wurzite oxy-nitrides were studied using density-functional theory (DFT) with the Linear Augmented Plane Wave (LAPW) method at varying dopant concentrations. Furthermore, these novel spinel photocatalysts were found to be active in degrading methylene blue in visible light and oxygen production from silver nitrate. The protocol developed opens a different avenue for the synthesis of semiconductors possessing the spinel crystal structure and with band gaps engineered to the visible region with potential applications for both opto-electronics and photocatalytic applications.

9:40am **EN+SS-FrM5 Synthesis and Surface Characterization of Nano-Scaled Structures for Energy Conversion Devices, W. Patterson, M. Robson, K. Artyushkova, P. Atanassov, University of New Mexico**

Using a microemulsion-based synthesis approach to create silica particles with internal porosity characterized by a nano-scale, bi-modal pore size distribution, we have developed functional templates for non-Platinum catalysts for fuel cell technologies. This material is derived from novel silica particles synthesized through oil/water/surfactant microemulsion templating under controlled conditions to have two distinct pore size regimes (~5 nm and ~40 nm). The larger pores, determined by the volume of microemulsion droplets, allow for more facile infiltration of precursors as compared to fumed silica previously used as the templating material. The smaller pores are determined by micellar dimensions and allow sites for creation of active site centers.

After formation of the silica, a subsequent carbon/active-site precursor co-impregnation process is followed by pyrolysis and etching. This leads to formation of open-frame structures of synthetic carbon supports decorated with the nano-phase metallic catalyst of choice. The resulting high surface area material is a bi-porous, carbonaceous matrix decorated with a low loading of non-precious metal. Last year, this effort resulted in demonstrating Pt/C catalysts for oxygen reduction. We have since focused efforts towards non-Pt precursors for pyrolytic formation of a nitrogen-

containing carbon backbone structure in combination with transition metals, Co and Fe.

Synthesis conditions, such as the amount of precursor, pyrolysis temperature, and etching conditions play an important role in formation of the porous structure of the resulting electrocatalyst. Well designed nanoporous structures can effectively minimize transport limitations, thus increasing the accessibility of the active sites by gas and electrolyte phases in the fuel cell active layer.

Thorough characterization including SEM, TEM, XRD, and XPS was performed. Detailed physisorption was performed to characterize the pore structure and surface area of the materials. A thorough analysis of the surface composition and structure as a function of pyrolysis temperature for the pyrolyzed Co-N precursor with sucrose was performed and high-resolution XPS spectra were acquired.

Using methodology previously developed for correlation of material structure to properties, we provide an enhanced characterization of composition and structure, identification of active sites, and some insight into the mechanism of reduction/oxidation reactions.

10:00am **EN+SS-FrM6 Enhancement of Visible-Light Photocatalytic Efficiency of TiO₂ Nanopowder by Anatase/Rutile Interface Formation.**
Y.J. Chen, C.S. Lin, National Dong Hwa University, Taiwan, Republic of China

In this article we report that the presence of anatase/rutile interface is essential on realization of visible-light photocatalytic ability of TiO₂ produced by the novel flat-flame chemical vapor condensation (FFCVC) method. Previous study shows that when nitrogen is replaced by argon as precursor carrier gas as well as quench gas in the FFCVC process, the synthesized TiO₂ nanopowder changes from anatase/rutile dual phases to anatase single phase. The UV-vis absorption spectra suggest that the synthesized TiO₂ with single anatase phase may still possess visible light absorption capability when the process parameters are carefully chosen. However, the photocatalytic efficiency drops to minimal value for the single-phase TiO₂ compared with that for dual-phase TiO₂. To confirm that the photocatalytic efficiency difference is caused by the formation of anatase/rutile interface, we synthesize the TiO₂ nanopowder using argon as carrier gas while using either nitrogen or argon as quench gas for comparison. Results show that when using nitrogen as quench gas, the TiO₂ powder is mostly anatase phase with minor rutile content, while when using argon as quench gas, the TiO₂ powder is almost anatase phase with hardly any rutile content. From the x-ray diffraction analysis, the grain size of anatase from both processes is similar, indicating that the choice of quench gas does not influence significantly on the nucleation process of the TiO₂ nanopowder. On the other hand, the use of nitrogen as quench gas does promote the formation of rutile phase, even though the rutile content is still minimal. This observation indicates that the nitrogen as quench gas does have some effect, although weak, on TiO₂ nanopowder during its final coalescence and growth stage. The visible-light photocatalytic experiment shows that even two powder samples are similar, the photocatalytic efficiency of TiO₂ with minor rutile content is significant while that of TiO₂ with single anatase phase is insignificant. Since the anatase from both processes is considered the same, the photocatalytic efficiency difference must be due to that minor rutile formation. Since the photocatalytic reaction occurs mostly on the anatase surface, the enhancement of photocatalytic efficiency by the formation of rutile phase leads to the conclusion that the anatase/rutile interface is the major cause for the efficiency enhancement. We will show the XPS, EPR, and XRD characterization of powders and discuss the materials science behind the phenomenon.

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