Surface Science
Room 104D - Session SS+HC-TuA
Photocatalysis and Photochemistry at Surfaces

Moderator: Arthur Utz, Tufts University

2:20pm **SS+HC-TuA1 Investigations of Surface Chemistry for Pyridine-catalyzed CO$_2$ Reduction on GaP***, C.X. Kronawitter, **Bruce Koel**,* Princeton University

The surface chemistry of N-containing heteroaromatics, molecular co-catalysts that enable the selective electrochemical reduction of CO$_2$ to fuels, is discussed. The presented experimental results focus on elucidating the role of the electrode surface in CO$_2$ reduction reactions that are co-catalyzed by pyridine. For this catalysis, exceptionally high selectivity for reduced fuels has been reported when the reaction occurs at the surface a GaP photocathode. For this reason, experimental emphasis is placed on assessing preferential adsorption sites and bonding interactions of adsorbates on surfaces of GaP. A surface science approach is used, whereby ultra-high vacuum conditions facilitate the fabrication of highly characterizable electrode-adsorbate systems. The use of single crystal surfaces permits analysis of surface chemistry independent of complicating factors such as grain boundaries and morphology. Surface-sensitive core-level and vibrational spectroscopy techniques, including high-resolution X-ray photoelectron spectroscopy, synchrotron-based photoemission, and high-resolution electron energy loss spectroscopy, are used to probe adsorbate-substrate and adsorbate-adsorbate interactions for pyridine, water, hydrogen, and carbon dioxide on GaP. Scanning tunneling microscopy was used to obtain molecular orbital-resolved images of adsorbed molecules. Conclusions from experimental results on these model systems are supported by calculations using density functional theory. This work assists in generating a molecular-level understanding of the heterogeneous processes important to the reaction mechanisms involved in the efficient photoelectrocatalytic generation of carbon-containing fuels with high energy densities.

2:40pm **SS+HC-TuA2 Photoreactivity of Benzoate Monolayers on TiO$_2$: Comparison of Anatase (001) and Rutile (110)***, **Erik Skibinski**, W.J.I. DeBenedetti, A. Song, A. Ortoll-Bloch, M.A. Hines,* Cornell University

The photoreactivity of organic self-assembled monolayers (SAMs) on TiO$_2$ surfaces is of considerable importance to applications such as dye-sensitized solar cells and photocatalytic environmental remediation. Despite extensive research, there remains little information about the reactivity of well characterized TiO$_2$ surfaces under ambient conditions. Here, we study the surface structure and photoreactivity of near-ideal benzoate monolayers prepared from dilute aqueous solutions and reacted at atmospheric pressure on anatase (001) and rutile (110) surfaces using scanning tunneling microscopy, infrared and x-ray photoelectron spectroscopies, and density functional theory.

We show that self-assembled monolayers of benzoate, an analogue of the organic linkage used in dye-sensitized solar cells, undergo rapid photodecomposition on both rutile (110) and anatase (001) under ultraviolet illumination in ambient and oxygen-rich conditions. Interestingly, while the two surfaces have similar, although not identical, reactivities, they differ in their reaction products, with the anatase polymorph producing a surface-bound ketene.

3:00pm **SS+HC-TuA3 Light-driven H$_2$ Generation using Multicomponent Semiconductor-metal Colloidal Nanorod Heterostructures***, **Tianquan Lian**,* Emory University **INVITED**

Quantum confined semiconductor nanocrystals have been widely investigated as light harvesting and charge separation components in photovoltaic and photocatalytic devices. The efficiency of these semiconductor nanocrystal-based devices depends on many processes, including light harvesting, carrier relaxation, charge separation and charge recombination. The competition between these processes determines the overall solar energy conversion (solar to electricity or fuel) efficiency. Compared with single component quantum dots (QDs), semiconductor nanoheterostructures, combining two or more materials, offer additional opportunities to control their charge separation properties by tailoring their compositions and dimensions through relative alignment of conduction and valence bands. Further integration of catalysts (heterogeneous or homogeneous) to these materials form multifunctional nanoheterostructures. Using CdSe/CdS/Pt, dot-in-rod nanorods(NRs) with Pt tips, as a model system, we are examining the mechanism of long-lived charge separation and H$_2$ generation in the presence of sacrificial electron donor. The rates of electron transfer, hole transfer and charge recombination are directly monitored by transient absorption and time-resolved fluorescence spectroscopy. In this talk, we will discuss the mechanism of exciton dissociation, the dependence of the rates of elementary charge transfer processes on the dimension (size and length) and band alignment in these materials, and how these rates affect the overall H2 generation efficiency.

4:20pm **SS+HC-TuA7 Quenching of Electron Transfer Reactions through Coadsorption: A Study of Oxygen Photodesorption from TiO$_2$(110)***, **Greg Kimmel**, N.G. Petrik, M. Shen, M.A. Henderson,* Pacific Northwest National Laboratory

Using temperature programmed desorption (TPD) and photon stimulated desorption (PSD), we show that coadsorbates of varying binding energies on the rutile TiO$_2$(110) surface exert a commensurate inhibiting influence on the hole-mediated photodesorption of adsorbed O$_2$. A variety of coadsorbates (Ar, Kr, Xe, N$_2$, CO, CO$_2$, CH$_4$, N$_2$O, acetone, methanol or water) were shown to quench O$_2$ photoactivity, with the extent correlating with the coadsorbate's gas phase basicity, which in turn determines the strength of the coadsorbate-Ti^{4+} bond. Coadsorbed rare gases inhibited the photodesorption of O$_2$ by ~10-25%, whereas strongly bound species (water, methanol and acetone) nearly completely inhibited O$_2$ PSD. We suggest that coadsorption of these molecules inhibit the arrival probability of holes to the surface. Band bending effects, which vary with the extent of charge transfer between the coadsorbate and the TiO$_2$(110) surface, are not expected to be significant in the cases of the rare gases and physisorbed species. These results indicate that neutral coadsorbates can exert a significant influence on charge transfer events by altering the interfacial dipole in the vicinity of the target molecule.

4:40pm **SS+HC-TuA8 Different Effects of Oxygen Adsorption on the Band Bending of TiO$_2$ Nanoparticles Studied by Photoluminescence Spectroscopy***, **Shiliang Ma**, M. Reish, Z. Zhang, I. Harrison, J.T. Yates, Jr.,* University of Virginia

By employing photoluminescence (PL) spectroscopy, it was found that oxygen adsorption on powdered TiO$_2$ changes the band bending of anatase in different ways. On the one hand, oxygen exposure leads to molecular chemisorption of oxygen molecules, which take up negative charge, but can be reversibly removed by ultraviolet photodesorption from the TiO$_2$ surface. Molecular chemisorption of oxygen molecules increases the upward band bending of TiO$_2$ and decreases the PL emission. On the one hand, oxygen can adsorb through irreversible reaction with defects, which occurs through an intermediate state of molecularly chemisorption, reducing the intrinsic upward band bending at the TiO$_2$ surface resulting in PL emission increase. Since band bending plays an important role in charge carrier migration to the surface, this finding that oxygen adsorption can have two different effects on the band bending of TiO$_2$ provides a new perspective on how oxygen and oxygen vacancies may modulate photocatalytic reaction efficiencies.

5:00pm **SS+HC-TuA9 Imaging Photodecomposition of Trimethyl Acetic Acid on Cross-linked (1 × 2) Rutile TiO$_2$(110)***, Y. Xia, K. Zhu, **Zhenrong Zhang**, K.T. Park,* Baylor University

Photoreactivity of reduced TiO$_2$ is important in photocatalytic applications. Cross-linked (1 × 2) rutile TiO$_2$(110) has been extensively studied, yet the exact atomistic model remains a point of contention. Employing a carboxylic acid as a probing molecule, we studied the structure of cross-linked (1 × 2) TiO$_2$(110) through the interaction of trimethyl acetic acid (TMAA) with various sites on the surfaces using *in situ* scanning tunneling microscopy (STM). We compared three specific atomistic models for (1 × 2) reconstructed TiO$_2$(110), Ti$_2$O$_3$, Ti$_2$O, and Ti$_3$O$_6$. The adsorption of TMAA on strands at room temperature strongly supports the Ti$_2$O model for cross-linked (1 × 2) reconstructed TiO$_2$(110). Photodecomposition of TMAA shows the dependence on the initial TMA coverage and O$_2$ pressure.

5:20pm **SS+HC-TuA10 Non-Fullerene Acceptors for Organic Photovoltaics: PTCDA versus C$_{60}$***, **Steven Robey**,* National Institute of Standards and Technology

Extensive development of new polymer and small molecule donors has helped produce a steady increase in the efficiency of organic photovoltaic (OPV) devices. However, OPV technology would benefit from the introduction of non-fullerene acceptors. Unfortunately, efforts to replace fullerenes have typically led to significantly reduced efficiencies. A number of possible explanations for reduced efficiencies with non-fullerene acceptors compared to fullerene acceptors have been suggested, including the formation of unfavorable morphologies in non-fullerene systems and/or favorable excitation/carrier delocalization in fullerenes. In addition, enhanced exciton dissociation associated with fundamental characteristics of the fullerene molecular electronic states has also been suggested. We employed time-resolved two-photon photoemission (TR-2PPE) to directly compare exciton dissociation at interfaces between zinc phthalocyanine (ZnPc) interfaces and the non-fullerene acceptor, perylene tetracarboxylic dianhydride (PTCDA) versus dissociation measured at the analogous interface with C_{60}, and thus help discriminate between these potential explanations. Exciton dissociation rates are comparable for phthalocyanine interfaces with both acceptors, allowing us to suggest a hierarchy for effects influencing higher efficiencies with fullerene acceptors.

5:40pm **SS+HC-TuA11 Use of Photoluminescence to Monitor Surface Chemistry of Metal Oxide Nanoparticles***, S. Kim, D. Somaratne,* ***James Whitten,*** University of Massachusetts Lowell

Many metal oxides nanoparticles are photoluminescent upon irradiation with ultraviolet light, with visible emission arising from surface states and surface defects. Because of the sensitivity of the surface to adsorption and electron transfer to and from even weakly adsorbed molecules, photoluminescece (PL) is proving to be a convenient method of monitoring chemisorption and physisorption. Experimental and theoretical results are presented related to adsorption of various gases and organic vapors on zinc oxide, zirconium oxide, and titanium dioxide nanoparticles toward the goal of correlating adsorption to PL changes. X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) and Raman spectroscopy measurements have been performed on metal oxide nanoparticles and single crystals to investigate whether chemisorption occurs at room temperature and the details of adsorbate bonding. These results are combined with density functional theory (DFT) calculations to understand how adsorption influences the PL changes. In addition to atmospheric gases, examples of adsorbates that have been examined include ammonia, methanethiol, methanol, benzene, and pyridine. This research provides a convenient method of monitoring adsorption and lays the foundation for optochemical sensing, in which metal oxides may serve as a new type of gas sensor.

6:00pm **SS+HC-TuA12 Exploring Pd Adsorption, Diffusion, Permeation, and Nucleation on Bilayer SiO_2/Ru as a Function of Hydroxylation and Precursor Environment: From UHV to Catalyst Preparation***,* ***William Kaden,*** University of Central Florida

The hydroxylation-dependent permeability of bilayer SiO_2 supported on Ru(0001) was investigated by XPS and TDS studies in a temperature range of 100 K to 600 K. For this, the thermal behavior of Pd evaporated at 100 K, which results in surface and sub-surface (Ru-supported) binding arrangements, was examined relative to the extent of pre-hydroxylation. Samples containing only defect-mediated hydroxyls showed no effect on Pd diffusion through the film at low temperature. If, instead, the concentration of strongly bound hydroxyl groups and associated weakly bound water molecules was enriched by an electron-assisted hydroxylation procedure, the probability for Pd diffusion through the film is decreased via a pore-blocking mechanism. Above room temperature, all samples showed similar behavior, reflective of particle nucleation above the film and eventual agglomeration with any metal atoms initially binding beneath the film. When depositing Pd onto the same SiO_2/Ru model support via adsorption of $[Pd(NH_3)_4]Cl_2$ from alkaline (pH 12) precursor solution, we observe notably different adsorption and nucleation mechanisms. The resultant Pd adsorption complexes follow established decomposition pathways to produce model catalyst systems compatible with those created exclusively within UHV despite lacking the ability to penetrate the film due to the increased size of the initial Pd precursor groups.

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