

Tuesday Afternoon, October 20, 2015

Surface Science

Room: 112 - Session SS+EN-TuA

Photocatalysis, Photochemistry, and Chirality at Surfaces

Moderator: Arthur Utz, Tufts University

2:20pm **SS+EN-TuA1 Photoemission of Electron from Diamond Into Water: Enabling Novel Electrochemical Reduction Reactions**, *Robert Hamers, D. Zhu, L.H. Zhang*, University of Wisconsin-Madison, *J. Bandy*, University of Wisconsin-Madison, *G.M. Nathanson, J.R. Schmidt*, University of Wisconsin-Madison

Diamond's unusual property of negative electron affinity has long been used to enhance electron emission in vacuum. Recently we have demonstrated that diamond's facile electron emission properties can also be extended to solid-liquid interfaces. Electron photoemitted from diamond into water lead to formation of solvated electrons, widely regarded as the chemist's perfect reducing agent. We demonstrate the inexpensive diamond thin films and diamond powder can be used as solid-state sources of electrons able to induce the reduction of N₂ to NH₃ and the selective reduction of CO₂ to CO. In this talk we will discuss the factors that influence electron emission into liquids, differences from emission into vacuum, and how electrons emitted into liquids can induce novel reduced chemistry not possible with traditional photocatalysts.

2:40pm **SS+EN-TuA2 STM Tip-Induced Desorption of TMAA from TiO₂(110): Model Study of a Photocatalytic Process**, *Denis Potapenko, R.M. Osgood, Jr.*, Columbia University

Titanium oxide is a versatile photocatalytic material with numerous applications in the areas related to utilization of solar energy. Scanning Tunneling Microscopy (STM) allows explorations on the single molecule basis thus providing important insight into the physical phenomena involved in photocatalysis. Our experiments examine the tip-induced chemistry of trimethyl acetic acid (TMAA) molecules adsorbed on TiO₂ rutile(110) surface; this system was chosen as a model for light-driven catalysis since it is easily imaged with STM and since this system has been the subject of many earlier studies of photo and thermal chemistry. In present work we study the electrical hole-driven desorption of TMAA molecules, initiated by the charges, injected from the STM tip. Different values of the flux and the energy of the excitation charges were achieved by the simultaneous control of the setpoint current and the bias voltage of the STM tunneling junction. The dynamics of the tip-induced desorption of TMAA was compared with the photo-induced dynamics of the same reaction. In the latter experiments the monochromated light from a UV lamp was used as the source of excitation. We show that there is a threshold energy for a hot hole below the edge of the TiO₂ valence band that is required for TMAA photo-desorption.

3:00pm **SS+EN-TuA3 Ultrafast Time-resolved Photoelectron Spectroscopy of Photocatalytic Surfaces**, *Hrvoje Petek, S. Tan, A. Argondizzo*, University of Pittsburgh **INVITED**

We investigate the ultrafast optical excitation and electron relaxation pathways for the clean and molecule covered rutile TiO₂(110) surface. Using high power, broadly tunable (2.9-4.6 eV), 20 fs noncollinear parametric amplifier excitation source, we perform multiphoton photoemission (mPP) spectroscopy of TiO₂ surface. The energy, momentum, and pump-probe delay time resolved mPP spectra provide information on the occupied and unoccupied density of states that participate in photoemission from the valence band or the Ti-3d defect states on reduced TiO₂ surfaces. We find a new bulk transition between the Ti-3d bands of t_{2g} and e_g symmetry, which dominates the photoemission process from the Ti-3d defect states below the conduction band minimum of TiO₂.¹ The 3D mPP spectra provide information on the phase and energy relaxation of photoexcited electrons and holes.² Adsorption of molecules introduces adsorbate-induced resonances,^{3,4} which can be excited by charge transfer excitation from the Ti-3d defect states. Metal nanoparticles grown on TiO₂ also open new photoemission pathways. We map out the energy and momentum distributions of the adsorbate and nanoparticle resonances as well as their relaxation dynamics.

1. Argondizzo, A.; Cui, X.; Wang, C.; Sun, H.; Shang, H.; Zhao, J.; Petek, H., Ultrafast multiphoton pump-probe photoemission excitation pathways in rutile TiO₂(110). *Phys. Rev B* **91**, 155429 (2015).

2. Cui, X.; Wang, C.; Argondizzo, A.; Garrett-Roe, S.; Gumhalter, B.; Petek, H., Transient excitons at metal surfaces. *Nat Phys* **10**, 505 (2014).

3. Onda, K.; Li, B.; Zhao, J.; Jordan, K. D.; Yang, J.; Petek, H., Wet Electrons at the H₂O/TiO₂(110) Surface. *Science* **308**, 1154 (2005).

4. Li, B.; Zhao, J.; Onda, K.; Jordan, K. D.; Yang, J.; Petek, H., Ultrafast interfacial proton-coupled electron transfer. *Science* **311**, 1436 (2006).

4:20pm **SS+EN-TuA7 Surface and Interface Properties of Photoelectrocatalysts for Solar Fuels**, *Bruce Koel, C.X. Kronawitter, P. Zhao, Z. Chen*, Princeton University

Experiments using well-defined model catalysts under controlled conditions and utilizing a range of spectroscopic techniques for characterization of surface and interface properties and the nature and reactivity of surface-bound species can greatly advance understanding of the structure and reactivity of photoelectrocatalysts for solar fuels. We report on several of our recent studies, which include investigations of the effects of dopant incorporation on the structural and chemical properties of the α -Fe₂O₃(0001) surface for water oxidation catalysis, facet-dependent activity and stability of Co₃O₄ nanocrystals towards OER, and the interaction of water with GaP(110), a semiconductor that is known to enable selective CO₂ reduction to methanol in aqueous solutions of CO₂ and nitrogen-containing heteroaromatics. For water oxidation on α -Fe₂O₃, we found that Ni doping in thin films of model catalysts caused a new termination for the films and induced formation of more stable surface-bound OH groups. For the Co₃O₄ system, we used the well-defined morphologies of nanocubes and nanooctahedra to demonstrate that the (111) surfaces vastly out-perform the (100) surfaces for OER activity (overpotential and current density). Finally we have spectroscopically identified *in situ* the surface-bound species on GaP(110) associated with exposure to water using ambient pressure photoelectron spectroscopy (APPEs). These observations on model systems afford further analysis and discussion of the role of surface-bound species in mechanisms for catalyzed water oxidation and CO₂ reduction.

4:40pm **SS+EN-TuA8 Improving Hematite-Based Solar Water Splitting by Surface Modification with Sn, Ti, and FeOOH**, *Anjali Patel, A.J. Abel*, Drexel University, *I. Garcia-Torregrosa*, Utrecht University, Netherlands, *B. Opanasont, J.B. Baxter*, Drexel University

Photoelectrochemical (PEC) water splitting with hematite (α -Fe₂O₃) photoanodes presents a promising route to sustainable energy production due to hematite's favorable bandgap, chemical stability, and widespread abundance. However, limitations arise from sluggish oxygen evolution reaction (OER) kinetics at the hematite-electrolyte interface, requiring a significant overpotential to induce photocatalysis. We report on the effects of Sn, Ti, and FeOOH surface treatments on hematite photoanodes to improve PEC performance by overcoming surface kinetic limitations. Thin film hematite photoanodes were fabricated by successive ionic layer adsorption and reaction (SILAR) of FeOOH on F:SnO₂-coated glass substrates, followed by annealing at 450 C to induce phase transition of FeOOH into hematite. Subsequent annealing at 775 C caused diffusion of Sn from the F:SnO₂ substrate through the hematite, resulting in 0.5at% Sn concentration at the photoanode surface. Current-voltage testing revealed that the presence of Sn in the hematite film significantly reduced the photocurrent onset potential, suggesting improved hole injection efficiency. Electrochemical impedance spectroscopy (EIS) revealed a reduction in the surface state charge transfer resistance (R_{ct,ss}) by 2 orders of magnitude, supporting the importance of interfacial kinetics. Hematite photoanodes doped with up to 10% Ti were also prepared by incorporating titanium into the SILAR deposition bath. Ti doping decreased the onset potential by 600 mV and significantly increased the plateau photocurrent density from 0.01 mA/cm² at 1.23 V vs. RHE for undoped hematite to nearly 0.6 mA/cm² for Ti-doped photoanodes. EIS showed that Ti-doping reduced the R_{ct,ss} at applied potentials ranging from 0.8 to 1.6 V vs. RHE, indicating a possible catalytic effect on the OER reaction at the photoanode surface. FeOOH films were deposited on the hematite photoanodes by an additional SILAR step, which reduced the photocurrent onset potential and increased the plateau photocurrent density by 20%. Unlike Ti, the FeOOH surface treatment exhibited little to no effect on the R_{ct,ss}, suggesting that FeOOH does not directly catalyze the OER. However, both the FeOOH treatment and Ti doping significantly increased the peak surface state capacitance, which may be attributed to an increase in density of charged states at the hematite surface, resulting in higher plateau photocurrent. Together, these treatments yield photocurrents that are 3x larger than previous reports using SILAR-deposited planar hematite films, offering promising opportunities to overcome challenges in PEC water splitting with hematite photoanodes.

5:00pm **SS+EN-TuA9 Metalation of a Polypyridine Macrocycle on Au(111): Preparation of a Water Reduction Catalyst on a Solid Substrate.** *Gerson Mette, D. Sutter, S. Schmidrig, B. Probst, R. Alberto, J. Osterwalder*, Universität Zürich, Switzerland

Within the search for new materials and methods for renewable energy resources, photocatalytic water splitting is a very promising field of study. In this framework, a polypyridine macrocycle was investigated which was already described in 1984 but only superficially examined [1]. It shares some similarities to porphyrins but with pyridyl subunits instead of pyrrol, hence the given trivial name: *pyrphyrin*. A high stability of the pyrphyrin and corresponding complexes is indicated due to its conjugation, planarity and cyclic nature. Furthermore, metal complexes based on pyrphyrin show promise as water reduction catalysts.

In this study, we examined the preparation of a pyrphyrin metal complex on a single crystalline surface in ultrahigh vacuum. In a first step, pyrphyrin coverages of approximately one monolayer and less, as determined by XPS measurements, were obtained by sublimation of the molecules on a Au(111) surface at room-temperature. By means of Low-Energy Electron Diffraction (LEED) and Scanning Tunneling Microscopy (STM), two distinct phases depending on the surface coverage were identified and structurally characterized. In a second step, deposition of Co metal at the level of 5% of a monolayer and subsequent annealing led to the formation of an almost complete monolayer of Co-ligated pyrphyrin molecules.

[1] S. Ogawa et al., *J. Am. Chem. Soc.* **1984**, 106, 5760-5762.

5:20pm **SS+EN-TuA10 Chiral Selective Chemistry Induced by Natural Selection of Spin-Polarized Electrons by DNA.** *Richard Rosenberg*, Argonne National Laboratory, *D. Mishra, R. Naaman*, Weizmann Institute of Science, Israel

Most biomolecules can be synthesized in two different mirror-image (chiral) shapes, namely two enantiomers. The enantiomers are recognized by their ability to rotate the polarization of linear polarized light either to the left (L) or to the right (D). In bio-organisms, sugars are always D and amino acids are always L. How this enantiomeric preference originated remains a mystery. Investigations into possible avenues of prebiotic chiral selectivity have been pursued since the time of Pasteur. Many investigations in this area have been devoted to pathways that involve preferential destruction of a particular isomer in an initially racemic (equal quantities of both enantiomers) mixture, through the interactions of chiral particles such as circularly polarized UV radiation or longitudinally spin polarized electrons. It has been shown that low energy (0 – 10 eV) spin polarized secondary electrons, produced by irradiation of a magnetic substrate, can induce chiral-selective chemistry in an adsorbed adlayer.^[1] Additional work has demonstrated that organized, double-stranded (ds) DNA, adsorbed on a gold substrate, acts as a natural spin filter for initially unpolarized, low energy (0 – 1.2 eV) electrons produced by UV irradiation of the substrate, resulting in net polarizations as high as 60%.^[2] Experiment and theory indicates that this spin filtering effect should be effective for higher energy ($E < 15$ eV) electrons as well.^[3] In the present study, we probe if low energy secondary electrons, produced by x-ray irradiation of a gold substrate, and transferred through the chiral monolayer, induce enantiomeric selective chemistry in an adsorbed adlayer. To test this, (R)- or (S)-epichloroydrin (C_3H_5ClO , Epi) was adsorbed on a self-assembled monolayer of 70 base pair long dsDNA. The secondary electron-induced reaction was monitored by following changes in the Cl 2p x-ray photoelectron spectroscopy spectra. By kinetic modeling of the reaction, quantum yields (QYs) were determined. For S-Epi the QY was ~16 % greater than for the (R) enantiomer, while the QYs were the same for the two enantiomers when they were adsorbed on bare Au.

[1] R. A. Rosenberg, M. Abu Haija, P. J. Ryan, *Phys. Rev. Lett.* **2008**, 101, 178301.

[2] a) B. Gohler, V. Hamelbeck, T. Z. Markus, M. Kettner, G. F. Hanne, Z. Vager, R. Naaman, H. Zacharias, *Science* **2011**, 331, 894-897; b) S. G. Ray, S. S. Daube, G. Leitus, Z. Vager, R. Naaman, *Phys. Rev. Lett.* **2006**, 96, 036101.

[3] R. A. Rosenberg, J. M. Symonds, V. Kalyanaraman, T. Markus, T. M. Orlando, R. Naaman, E. A. Medina, F. A. López, V. Mujica, *J. Phys. Chem. C* **2013**, 117, 22307-22313.

5:40pm **SS+EN-TuA11 Creating Enantioselective Surfaces: Templating and One-to-one Interactions.** *Wilfred Tysoe*, University of Wisconsin-Milwaukee

The mode of operation of heterogeneous chiral modifiers can be classified into those operating as templates, where several modifier molecules act in concert to define a chiral adsorption site, or one-to-one modifiers that form a docking complex between the modifier and a prochiral reactant.

Enantioselectivity is measured by adsorbing chiral probe molecules onto chirally modified surfaces. Templating is illustrated using aminoacids on

Pd(111). Scanning tunneling microscopy (STM) reveals that some aminoacids form tetrameric units, and others form dimers. Only those aminoacids that form tetramers are enantioselective implying that the tetramers act as templates.

Naphthylethylamine (NEA) is proposed to act as a one-to-one modifier. The interaction between NEA and a prochiral reactant, methyl pyruvate, is explored using STM. Possible docking complexes are identified using density functional theory and the simulated images are compared with experimental images. Finally, it is shown the tartaric acid on Pd(111) acts as a one-to-one modifier for glycidol and is controlled by hydrogen-bonding interactions.

6:00pm **SS+EN-TuA12 Single-Molecule and Single-Active-Site Studies of Stereocontrol by Chemisorbed Chiral Molecules.** *Peter McBreen, Y. Dong, J.C. Lemay, G. Goubert*, Laval University, Canada, *M.N. Groves, B. Hammer*, Aarhus University, Denmark

Isolated adsorbed chiral molecules can stereodirect prochiral co-adsorbates on reactive metal surfaces and the application of this phenomenon underpins a method to perform asymmetric heterogeneous catalytic reactions. Typically, the stereochemical action is attributed to intermolecular interactions in complexes formed by docking the prochiral substrate in a chiral pocket created by the chemisorbed chiral molecule. We will present results from combined variable temperature STM and optB88-vdW DFT studies of individual bimolecular docking complexes formed by enantiopure 1-(1-naphthyl)ethylamine and selected prochiral molecules on Pt(111). The experiments reveal sub-molecularly resolved and time-resolved site-specific and stereospecific data. The results show that a single chemisorbed enantiomer simultaneously presents several chiral pockets, each displaying a specific prochiral ratio for a given substrate molecule. A hierarchy of metal-molecule and molecule-molecule interactions is found to control prochiral selection at each site. Time-lapsed STM measurements of individual substrate molecules sampling a set of chiral pockets provide new insight on the dynamics of stereocontrol.

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