

Wednesday Morning, October 21, 2015

Surface Science

Room: 112 - Session SS-WeM

Environmental Interfaces, Ambient Surfaces, In-Operando Studies and Adsorption on 2D Materials

Moderator: Peter Sutter, University of Nebraska - Lincoln

8:00am **SS-WeM1 Liquid-Jet Ambient Pressure Photoelectron Spectroscopy Studies of the Liquid/Vapor Interface of 1-Propanol and 2-Propanol Aqueous Solutions**, *Michael Makowski, J.M. Langford, D. Tobias, J.C. Hemminger*, University of California Irvine

The liquid/vapor interface of aqueous 1- and 2-propanol solutions for a broad range of concentrations was studied using a liquid-jet ambient pressure X-ray Photoelectron Spectroscopy system at the Advanced Light Source synchrotron in the Lawrence Berkeley National Laboratory. At low concentrations, 1-propanol displays a clear propensity to lie at the solution surface, evidenced by an enhanced carbon 1s XPS signal for electrons of low kinetic energy. Near a concentration (mole fraction) of 0.01 mf, a surface layer of 1-propanol appears to saturate, as evidenced by the saturation of the carbon 1s to oxygen 1s XPS signal ratio. Furthermore, over increasing concentrations carbon and oxygen 1s binding energies show a sharp redshift of 1 eV, until reaching a concentration of approximately 0.01 mf. This suggests an increasing 1-propanol density at the surface, with the resulting surface dipole layer causing a shift in the observed C1s and O1s binding energies for the condensed species.

These results of aqueous 1-propanol are compared and contrasted to similarly obtained aqueous 2-propanol carbon and oxygen spectra. Moreover, experimental results were corroborated with classical molecular dynamics simulations. Density profiles relative to an instantaneous interface were calculated for aqueous 1-propanol solutions. MD simulations indicate that 1-propanol accumulates at the surface at very low concentrations and a surface layer saturates at approximately 0.01 mf in agreement with the experimental results.

8:20am **SS-WeM2 Near Ambient Pressure XPS at the SLS – In Situ Cell Design for Solid/Vapor Interfaces and First Results in Environmental TiO₂ Photocatalysis**, *Fabrizio Orlando*, Paul Scherrer Institut, Switzerland, *A. Waldner*, Paul Scherrer Institut and ETH Zürich, Switzerland, *M.-T. Lee*, Paul Scherrer Institut and University of Bern, Switzerland, *M. Birrer*, *T. Bartels-Rausch*, Paul Scherrer Institut, Switzerland, *C. Proff*, Paul Scherrer Institut and ETH Zürich, Switzerland, *T. Huthwelker*, *A. Kleibert*, Paul Scherrer Institut, Switzerland, *J. van Bokhoven*, Paul Scherrer Institut and ETH Zürich, Switzerland, *M. Ammann*, Paul Scherrer Institut, Switzerland

Near ambient pressure X-ray photoelectron spectroscopy (NAPP) is a powerful tool to investigate elemental composition and chemical specificity of surfaces under reaction conditions that offers tremendous opportunities in environmental science and heterogeneous catalysis research. In the first part of this contribution I will provide a brief outlook on a new analysis chamber for the NAPP endstation at the Swiss Light Source that is designed for in situ XPS and NEXAFS at solid/vapor interfaces under environmentally relevant conditions of temperature and pressure (up to 20 mbar and 100% relative humidity) [1]. The flow-tube design of this new chamber allows to perform in situ measurements at high pressure and UHV conditions one after the other in the same analysis cell, while at the same time reducing the exposed volume and surface area of the analysis cell. Moreover, this chamber features (i) a direct access from a gas dosing system down to the sample, allowing for the admission of sticky gases with reduced wall effects, and (ii) a UV laser setup, providing the opportunity to investigate photoactive materials under atmospherically relevant conditions of pressure and light with reduced extent of gas phase photochemistry induced by the UV-light. We have used this novel chamber to investigate photocatalysis on TiO₂, which is a component of natural mineral dust that represents an important reactive aerosol in the atmosphere affecting the ozone budget and the climate. In this context, adsorption of water and hydroxylation of the surface, which are key aspects to understand TiO₂ photocatalysis in the environment, offer still major open questions. Earlier NAPP studies have provided important insight into the nucleation of water on this surface [2]. In a recent study we have quantified the effect of humidity on ozone-induced band bending on the TiO₂(110) surface [3], and found interesting changes in XPS and NEXAFS spectra indicative of changes in the hydrogen bonding structure in multilayers of water [4]. I will discuss our most recent NAPP investigation on the influence of UV light and humidity on the adsorption of water on a TiO₂ powder sample surface. Our results indicate an enhancement of water adsorption under UV irradiation, which might be

the basis to explain light-induced superhydrophilicity previously observed on TiO₂-based nanomaterials. I will also briefly illustrate an application study on the uptake of trace gases on ice surface.

References

- [1] F. Orlando et al., submitted.
- [2] G. Ketteler et al., *J. Phys. Chem C* 111, 8278 (2007).
- [3] M. Lampimäki et al., *ChemPhysChem* 14, 241 (2013)
- [4] M. Lampimäki et al., *J. Phys. Chem. C* 119, 7076 (2015).

8:40am **SS-WeM3 Ambient Pressure XPS Observation of Electrode Surfaces During Electrochemical Reactions**, *Hirohito Ogasawara, S. Kaya, H.S. Sanchez Casalongue, M.L. Ng, D. Friebe, A. Nilsson*, SLAC National Accelerator Laboratory

We have been focusing on identifying the surface electronic structure and chemical nature of catalytic electrodes during electrochemical reactions through the use of synchrotron-based ambient pressure photoemission spectroscopy (APXPS) [1]. One of the crucial factors that limit electrochemical water splitting is the large overpotential required for the oxygen evolution reaction. Iridium oxide, which is one of the most widely used anode catalyst, has been shown to have high activity and stability in water electrolysis. APXPS studies indicate both oxide and hydroxide species on the catalyst surface. Under electrochemical oxygen evolution conditions, iridium undergoes a change in oxidation state, which takes place predominantly at the surface of the catalyst [2]. Molybdenum sulfides are promising materials in the search for cost-effective cathode catalyst. We tracked the transformation of amorphous MoS₃ nanoparticles during electrochemical hydrogen evolution reactions. We observed that surface sites are converted from MoS₃ to MoS₂ increasing MoS₂ edge-like sites with high activity [3]. The sluggish kinetics in oxygen reduction reaction is one of the key challenges in polymer electrolyte membrane fuel cells. We established that the species on the platinum catalytic electrode change drastically depending on the oxygen pressures. We used this knowledge to clarify that the reaction pathway is dependent on the operating conditions [4].

References

- [1] S. Kaya, H. Ogasawara, L.-Å. Näslund, J.-O. Forsell, H. Sanchez Casalongue, D.J. Miller, A. Nilsson, *Catalysis Today* 205 (2013) 101
- [2] H. Sanchez Casalongue, M.L. Ng, S. Kaya, D. Friebe, H. Ogasawara, A. Nilsson, *Angewandte Chemie* 126 (2014) 7297
- [3] H. Sanchez Casalongue, J.D. Benck, C. Tsai, R.K.B. Karlsson, S. Kaya, M.L. Ng, L.G.M. Pettersson, F. Abild-Pedersen, J.K. Nørskov, H. Ogasawara, T.F. Jaramillo, A. Nilsson, *J. Phys. Chem. C* 118 (2014) 29252
- [4] H. Sanchez Casalongue, S. Kaya, V. Viswanathan, D.J. Miller, D. Friebe, H.A. Hansen, J.K. Nørskov, A. Nilsson, H. Ogasawara, *Nature Communications* 4 (2013) 2817

9:00am **SS-WeM4 Formation of Heterogeneous Multiple-Oxide/Hydroxide Species on a GaP(111) Surface Tracked by In Situ Near-Ambient Pressure XPS**, *Xueqiang Zhang, S. Ptasinska*, University of Notre Dame

A photoelectrochemical (PEC) solar cell for water splitting converts solar energy into chemical energy and store it in the form of hydrogen, which is a promising candidate of sustainable and clean fuels. PEC solar cells consisted of phosphide-based III-V semiconductors are known to have a higher solar to hydrogen conversion efficiency than other materials. They are, however, usually limited by technological drawbacks such as photocorrosion or decreased electron extraction efficiency due to the formation of surface oxide species. The formation of surface oxides becomes critical when operating electrodes are exposed to aqueous electrolytes or to ambient conditions. Therefore, it is desirable to understand the interfacial processes of water interactions with semiconductors, and to elucidate possible oxidation and reduction mechanisms at the H₂O/semiconductor interface, especially under near realistic conditions.

In this study, water dissociative adsorption onto a GaP (111) surface was investigated using near ambient pressure X-ray photoelectron spectroscopy (NAP XPS) at various pressures and temperatures [1]. This advanced technique allowed us to monitor the H₂O/semiconductor interfacial chemistry under *operando* conditions, which would not be feasible to be investigated by traditional surface sensitive techniques. The interfacial chemistry was tracked by recording high-resolution photoemission spectra of Ga 2p_{3/2}, O 1s, and P 2p. In the pressure-dependent study conducted at room temperature, ~300 K, the enhancement of surface Ga hydroxylation and oxidation was observed with an increase in H₂O pressures. This finding was also confirmed by changes observed in the photoemission spectra of O

1s. In the temperature dependent study, surface Ga hydroxylation and oxidation were further enhanced at temperatures below 673 K. While a large-scale conversion of surface O-Ga-OH species into Ga hydroxide, along with surface P oxidation, were observed at 773 K. Moreover, the formation of Ga and P oxide/hydroxide networks was suggested and a "phase diagram" that demonstrates the distribution of different chemical species under various experimental conditions has been generated (supplemental document). Our results led to a better understanding of the H₂O/semiconductor interfacial chemistry and the water splitting mechanism in the PEC solar cells.

Reference

1. Zhang, X., Ptasinska, S. Distinct and dramatic water dissociation on GaP(111) tracked by near-ambient pressure X-ray photoelectron spectroscopy. *Phys. Chem. Chem. Phys.*, 2015, 17, 3909-3918.

9:20am **SS-WeM5 Investigation of Liquid/Solid Interfaces using Photoelectron Spectroscopy, Hendrik Bluhm**, Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

Solid/vapor, liquid/vapor and liquid/solid interfaces govern many processes in the environment, heterogeneous catalysis, and technology. Ambient pressure photoelectron spectroscopy is an excellent method for the characterization of these interfaces under operating conditions, in particular since it affords to correlate the elemental and chemical composition at the interface with the electrical potentials. This talk will focus on the application of APXPS to the investigation of liquid/solid surfaces under realistic conditions, which is arguably the next frontier in surface science. We will highlight the application of ambient pressure XPS in combination with standing waves for the investigation of the electric double layer at solid liquid interfaces in environmental science and corrosion chemistry.

11:00am **SS-WeM10 Surface and Bulk Crystallization Kinetics of Amorphous Solid Water Nanoscale Films, R. Scott Smith, C. Yuan, R.A. May, B.D. Kay**, Pacific Northwest National Laboratory

We investigate the crystallization kinetics of nanoscale amorphous solid water (ASW) films using temperature-programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). ASW is a metastable form of water created by vapor deposition on a cold substrate ($T < 130$ K). In prior work, we reported the episodic release of trapped gases in concert with the crystallization of ASW, a phenomenon that we termed the "molecular volcano." The observed abrupt desorption is due to the formation of cracks that span the film to form a connected pathway for release. In a recent study we used the selective placement of an inert gas layer is used to show that cracks form near the top of the film and propagate downward into the film. Those experiments showed that, after some induction time, cracks propagate linearly in time with an Arrhenius dependent velocity consistent with the crystallization growth rates reported by others. This suggested a direct connection between the crystallization growth and the crack propagation rate. In the present study we directly measure the surface (using TPD) and bulk (using RAIRS) ASW crystallization kinetics as a function of film thickness. These results show that nucleation and crystallization begins at the ASW/vacuum interface and then the crystallization growth front propagates linearly into the bulk. The details of the experiment and the interpretation of the results will be discussed in detail.

This work was supported by the US Department of Energy, Office of Science (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. The research was performed using EMSL, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated by Battelle operated for the DOE.

11:20am **SS-WeM11 Environmental Effects on Oxidative Surface Passivation Across Al_xFe_yNi_{1-x-y} Composition Space, Matthew Payne, J.B. Miller, A.J. Gellman**, Carnegie Mellon University

Alloys that derive robust oxidation resistance by the preferential formation of a passivating Al₂O₃ scale are commonly used for structural applications in thermochemically harsh operating environments. Often, one of the primary design concerns is to determine the lowest Al content required to induce passivation, so as to minimally impair the mechanical properties of the material. This "critical Al concentration" is kinetically dictated and can depend strongly on both multicomponent composition and the nature of the oxidizing environment. We have previously developed high-throughput methodology to study oxidation using composition spread alloy films (CSAFs), combinatorial sample platforms with continuous lateral composition gradients. Behavior related to oxidative corrosion and passivation can be characterized continuously across an entire ternary composition space with a single CSAF, using a combination of spatially resolved techniques including optical imaging, scanning electron microscopy, energy-dispersive X-ray spectroscopy, Raman spectroscopy,

and X-ray photoemission depth profiling. We have used this methodology to compare the oxidation of Al_xFe_yNi_{1-x-y} alloys at 700 K in dry-air and humid-air environments. The critical Al concentration in the Fe-rich region of composition space was found to be significantly higher for exposure to the humid air. The continuous nature of the results provides valuable fundamental insight into the interplay of composition and environment on alloy oxidation kinetics.

11:40am **SS-WeM12 Hydrogen-Bonded Self-Assembled Molecular Structures on Hexagonal Boron Nitride, Vladimir Korolkov, S. Svatek, L. Yang, J. Kerfoot, A. Summerfield, N. Champness**, University of Nottingham, UK, *T. Taniguchi, K. Watanabe*, The National Institute for Materials Science, Japan, *N. Besley, P. Beton*, University of Nottingham, UK

Hexagonal boron nitride (h-BN) is a layered material and a wide-gap semiconductor with a band gap of 5.2 eV. The latter property makes it highly attractive as a support to study optical and electrical properties of monolayered molecular assemblies stabilized by non-covalent interactions. Although h-BN has been known since 1940s it is a relatively new substrate in the area of molecular self-assembly. In part this is due to the widespread use of scanning tunneling microscopy to acquire images of molecules, but this technique is not compatible with h-BN.

The adsorption of a range of molecules on BN and other layered materials has been investigated using high resolution atomic force microscopy (AFM). We have observed several arrangements of molecules which are stabilized by hydrogen bonding including a bimolecular layer formed by perylene tetracarboxylic di-imide (PTCDI) and melamine which form an open nanoporous array in which the planar PTCDI molecules are adsorbed parallel to the substrate. The networks are deposited from solution by immersion of BN substrate and the ordering may be improved by post-annealing in an inert atmosphere. We have also investigated the adsorption of 5,10,15,20-tetrakis(4-carboxylphenyl)porphyrin (TCPP), a dye molecule with a planar porphyrin macrocycle as its core. This molecule forms an open square array, also stabilized by hydrogen bonding through carboxylic acid pendant groups which steer the arrangement so that macrocycle lies parallel to the surface. In this arrangement the molecular layer is strongly fluorescent showing lines which are red-shifted from solution. When molecules are adsorbed on MoS₂ they form similar structures but the resulting islands are smaller and less ordered, and, due to the smaller band gap of MoS₂, fluorescence is quenched. We also present density functional theory calculations of the conformation of adsorbed molecules and numerical estimates of the hydrogen bonding and adsorption energies. We discuss this approach as a route to the molecular functionalization of two-dimensional materials and the formation of hybrid molecular devices.

The work will present an outstanding examples of single molecule and submolecular resolution achieved in the ambient on standard Atomic Force Microscopes. Most of the presented results will be on level with the published UHV-STM studies.

12:00pm **SS-WeM13 Suppression of the Topological Surface State of Bi₂Te₃ by the Organic Molecule Manganese Phthalocyanine, Andrew Hewitt, J. Boltersdorf, P.A. Maggard, D.B. Dougherty**, North Carolina State University

Organic molecules coupled to the spin-textured topological surface states of a topological insulator (TI) are expected to result in an interface ideal for organic spintronic devices.¹ Exploiting interfacial control at molecule-functionalized TI surface is a crucial step in realizing the potential of these new materials. It has been shown² that such a coupling may exist, along with a new hybrid-interface state above the Fermi level, between the magnetic molecule Manganese Phthalocyanine (MnPc) and the TI Bi₂Te₃. We report the suppression of the topological surface state by the adsorption of MnPc molecules as measured by Ultraviolet Photoelectron Spectroscopy. We show a new state emerging below the Fermi level at less than a monolayer coverage of MnPc molecules. The new interface state is different than the topological surface state and the molecular orbitals of the MnPc molecules as evidenced by the modified dispersion with Angle-Resolved Photoelectron Spectroscopy. We also observe an *n*-doping effect as charge is transferred from the molecule to the TI substrate in agreement with recent work.^{2,3} We suggest that this interface system may have important implications for understanding the role of local time reversal symmetry breaking in TI's and in controlling spin injection into these novel materials.

[1] Jakobs *et al.* DOI: 10.1021/acs.nanolett.5b02213

[2] Sessi *et al.* Nano Lett. 2014, 14, 5092–5096

[3] Bathon *et al.* Nano Lett. 2015, 15, 2442–2447

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