Thursday Afternoon, October 21, 2010

Surface Science
Room: Picuris - Session SS-ThA

Environmental Interfaces
Moderator: H. Fairbrother, Johns Hopkins University

2:00pm **SS-ThA1 Environmental Interfaces: Where the Vacuum, Cleanliness, and Size Gaps Must Be Minimized**, *G. Brown, Jr.,* Stanford University, *S. Yamamoto,* University of Tokyo, Japan, *T. Kendelewicz,* Stanford University, *J. Newberg, H. Bluhm, M. Salmeron,* Lawrence Berkeley National Laboratory, *A. Nilsson,* Stanford Synchrotron Radiation Lightsource, *Y. Wang, M. Michel,* Stanford University, *Y. Choi, P. Eng,* University of Chicago, *J. Ha,* University of California at Berkeley, *A. Spormann,* Stanford University **INVITED**
Environmental interfaces come in many varieties, including solid-water, solid-gas, solid-microbial biofilm-water, solid-organic film-water, etc., and they exist under a variety of conditions, none of which involve UHV. In addition, the solids involved in environmental interfaces are often in the nanoparticle size range, which may result in properties, such as surface structures and reactivities, that differ from their bulk counterparts. Another common complication is that the surfaces of environmental solids are often coated by natural organic matter and/or microbial biofilms, which could have dramatic effects on their surface charge properties, extent of aggregation, and reactivity. In contrast, most surface science studies involve clean single crystal surfaces on which metals, molecules, or organic molecules are attached under carefully controlled conditions, typically involving UHV. In order to increase our understanding of the chemical and biological processes at environmental interfaces, the pressure, cleanliness, and size gaps must be overcome to the extent possible in surface science studies. We will discuss recent near-ambient pressure XPS studies of the interfaces between alpha-Fe2O3 (0001) and water and Fe3O4 and water, which have revealed the extent of dissociation of water and hydroxylation of these surfaces. We will also present the results of new x-ray standing wave fluorescence yield spectroscopy studies of the interaction of aqueous metal ions with alpha-Fe2O3 nanoparticles coated by polyacrylic acid and natural organic matter thin films as well as with microbial biofilm-coated single crystal metal oxides. The results of these studies have revealed that the intrinsic order of reactivities of different metal oxide surfaces coated by organic matter or microbial biofilms is not affected by the coatings. However, time-dependent studies have shown that the rates of partitioning of metal ions between aqueous solutions and metal oxide surfaces are diffusion controlled. Finally, we will discuss differences in surface structures of nanoparticulate (avg. diameter = 10 nm) vs. microparticulate (avg. diameter = 550 nm) of alpha-Fe2O3 derived from XAFS spectroscopy studies of Zn(II) ions sorbed on the particle surfaces.

2:40pm **SS-ThA3 Ion Segregation and Deliquescence of Alkali Halide Nanocrystals on SiO2 Revealed by Scanning Polarization Force Microscopy**, *K. Arima,* Osaka University, Japan, *P. Jiang,* Lawrence Berkeley National Laboratory, *D.-S. Lin,* National Tsing Hua University, Taiwan, Republic of China, *A. Verdaguer,* CSIC-ICN, Spain, *H. Bluhm, M. Salmeron,* Lawrence Berkeley National Laboratory
The adsorption of water on alkali halide (KBr, KCl, KF, NaCl) nanocrystals on SiO2 and their deliquescence was investigated as a function of relative humidity (RH) from 8% to near saturation by scanning polarization force microscopy (SPFM). SPFM is a noncontact AFM operation mode based on electrostatic forces, which gives two images (topographic image modulated by a local dielectric constant and surface potential image) simultaneously. At low humidity water adsorption solvates ions at the surface of the crystals and increases their mobility. This results in a large increase in the dielectric constant, which is manifested in an increase in the electrostatic force and in an increase in the apparent height of the nanocrystals. Above a critical RH (58% RH in the case of KBr nanocrystals) the diffusion of ions leads to Ostwald ripening, where larger nanocrystals grow at the expense of the smaller ones. At the deliquescence point droplets were formed. For KBr, KCl and NaCl, the droplets exhibit a negative surface potential relative to the surrounding region, indicative of the preferential segregation of anions to the air-solution interface. We will also show spectra obtained by ambient pressure X-ray photoelectron spectroscopy to complement the SPFM results.

3:00pm **SS-ThA4 Investigation of H/D Exchange in Water Layers on Hydrophilic/Hydrophobic Organic Surfaces**, *N.M. Barrentine, R.L. Grimm, J.C. Hemminger,* University of California, Irvine
Water interactions with organic surfaces are of great importance to chemistry in the environment as well as a variety of device manufacturing and performance issues. We have carried out studies of the interaction of D2O with organic surfaces as a function of the hydrophilic/hydrophobic nature of the surface. Temperature programmed desorption (TPD) experiments are used to follow the strength of the interaction of adsorbed D2O with the surface and to follow the extent of H/D exchange that occurs on the surface. Self-assembled monolayers (SAM) of alkanethiols on Au(111) surfaces are used as a highly characterized organic surface. Hydrophilic SAMs are generated using 6-mercapto-1-hexanoic acid ($HSC_5H_{10}COOH$) on Au(111). Similarly, hydrophobic SAMs are generated using 1-octanethiol ($HSC_7H_{14}CH_3$). TPD experiments were carried out following adsorption of D2O on the SAM surface at a temperature of 120 K. H/D exchange was observed by simultaneously monitoring m/z = 20 (D_2O^+), 19 (HDO^+), and 18 (OD^+ and H_2O^+) in the TPD experiments. Our experiments showed an increase in the m/z 19/20 ratio for experiments with the hydrophilic SAM in comparison to the hydrophobic SAM, indicative of H/D exchange with the acidic proton of the 6-mercapto-1-hexanoic acid SAM. Results will also be presented for mixed hydrophilic/hydrophobic monolayers as a function of the hydrophilic/hydrophobic ratio.

3:40pm **SS-ThA6 Photochemistry of O2 on Reduced Rutile TiO2(110)**, *G.A. Kimmel, N. Petrik,* Pacific Northwest National Laboratory
We investigate the adsorption and photon-stimulated reactions of O2 on reduced, rutile TiO2(110). After adsorption at 28 K and annealing to 100 K, at least 85% of the O2 has not dissociated. Typically, less than 50% of this molecularly adsorbed O2 desorbs via hole-mediated reactions during irradiation with ultraviolet (UV) photons. However, UV irradiation dissociates ~20 – 45 % of the chemisorbed O2, which we propose to occur through electron attachment reactions. In addition, weakly bound (physisorbed) O2 readily reacts with chemisorbed O2 during UV irradiation. A simple model based on the oxygen coverage and the charge of the chemisorbed oxygen, which accounts for the observations, is presented. These results show that the photochemistry of oxygen on TiO2(110) is both diverse and more complicated than previously appreciated.

4:00pm **SS-ThA7 Pentagons and Heptagons in the First Water Layer on Pt(111)**, *S. Nie, P.J. Feibelman, N.C. Bartelt, K. Thürmer,* Sandia National Laboratories
We present STM observations of the first layer of water on Pt(111). Because scanning parameters typically used for high-resolution imaging can easily disturb the fragile water layer, acquiring images is particularly challenging. Nonetheless, employing an extremely small tunneling current, we were able to extract enough structural detail to decipher how individual water molecules arrange themselves.

At a growth temperature of 140K, we found large regions consisting of the √37 and √39 phases previously observed in diffraction experiments [1]. The main characteristic of both are triangularly-shaped regions, which appear as depressions in STM. The triangles are embedded in a hexagonal lattice of water molecules, which, remarkably, is rotated by approximately 30° relative to the √3x√3-R30° structure that is the usual starting point for discussions of ice films. We propose that the triangular regions consist of a central hexagon of water molecules surrounded by alternating pentagons and heptagons. Twelve water molecules in the center of this ("575757" di-interstitial) defect lie approximately flat, with O atoms directly atop Pt atoms. Elsewhere, the water molecules lie "H-down," i.e., with an H atom beneath the O. Image simulations based on DFT calculations are consistent with this non-conventional model.

The dramatic structural differences between the √39 phase and 3-D ice consisting of stacked unrotated classic bilayers suggests that 3-D islands do not grow on top of the wetting layer, rather the wetting-layer molecules substantially rearrange when 3-D ice nucleates.

[1] For example, A. Glebov, A. P. Graham, A. Menzel and J. P. Toennies, J. Chem. Phys. **106**, 9382 (1997).

4:20pm SS-ThA8 Wetting Monolayer Structure on Metals, *P.J. Feibelman*, *N.C. Bartelt*, Sandia National Laboratories

The $\sqrt{37}$ and $\sqrt{39}$ rotated H_2O-molecule adlayers that form at low T on Pt(111) have been a mystery since 1997. [1] Their structures must optimize among : 1) forming as many H-bonds as possible, 2) allowing the maximum number of H_2O's to lie flat, with O-atoms in atop sites, and 3) minimizing strain in bond lengths and angles. But, 1) rules out vacancy structures, 2) begs why rotation, leaving few O atoms in atop sites, would be preferred, and 3) is troublesome in the models proposed in Ref. 1, given their areal compression relative to ordinary ice.

Haq, et al. spun off a clue in an effort to interpret a spectroscopically observed metastable water monolayer on Ru(0001). Flat-lying molecules that have each other as neighbors can lie closer to the metal than in the conventionally imagined "ice-like" adlayer, where adjacent molecules' dangling H-bonds force the flat molecules up. [2] Thus, they proposed a water layer on Ru(0001) comprising chains of flat H_2O molecules separated by molecules whose dangling H-bonds point toward the metal. Elaborating, we find that a *checkerboard* of compact flat-lying and H-down phases is even somewhat better bound, and this, together with new, telling STM images, has led us to plausible, low-energy structures for water on Pt(111).

STM images of these structures show $\sqrt{37}$ and $\sqrt{39}$ arrays of dark triangles separated by ribbons of H_2O-molecule hexagons. [3] We assign the triangles to di-interstitial molecular "defects," wherein six flat-lying H_2O's, with O atoms ~2.2Å directly atop Pt's, anchor the water layer to the metal. In DFT calculations, these "defect" structures, containing three 5-member and three 7-member rings of H_2O molecules, have lower energy than any purely hexagonal mesh. A competing explanation of the dark triangles as vacancy islands [4] is significantly less bound, because of its many dangling bonds. Remarkably, analogous 555777 structures on Ru(0001), never observed, are better bound than any purely hexagonal structure tried to date.

[1] A. Glebov, et al., J. Chem. Phys. 106, 9382(1997).

[2] S. Haq, et al., Phys. Rev. B73, 115414 (2006).

[3] S. Nie, et al, unpublished.

[4] S. Standop, et al., unpublished.

4:40pm SS-ThA9 Experimental Evidence for Mixed Dissociative and Molecular Adsorption of Water on a Rutile TiO_2(110) Surface without Oxygen Vacancies, *L.E. Walle*, *A. Borg*, Norwegian University of Science and Technology, *P. Uvdal*, Lund University, Sweden, *A. Sandell*, Uppsala University, Sweden

Rutile TiO2(110) has for many years been regarded as the benchmark surface for fundamental studies of metal oxide surface chemistry. Since water is an integral part of the environment, the H2O/TiO2(110) system has received more attention than any other comparable system [1,2]. While the dissociation of water on the oxygen deficient TiO2(110) surface has been characterized in detail, there is as of yet no consensus reached between experimentalists and theorists regarding a very fundamental question: Does water dissociate upon adsorption on the defect-free TiO2(110) surface?

We have studied the interaction of water with the rutile TiO2(110) surface using synchrotron radiation photoemission at beamline D1011 at the MAX-lab synchrotron radiation source, and in this contribution we demonstrate that O 1s spectra recorded at grazing emission angle at optimized photon energy in conjunction with valence spectra allow for the observation of OH on the surface even when substrate oxygen is present. The surface was prepared free from oxygen vacancies following the recipe in ref. [3].

Here we find evidence for mixed molecular and dissociative water adsorption at monolayer coverage on the rutile TiO2(110) surface free from oxygen vacancies. At monolayer coverage the OH:H2O ratio is close to 0.5 and reducing the coverage by heating yields an increased OH:H2O ratio. At room temperature neither species originating from the monolayer on the defect free surface can be detected. The OH species of the monolayer hence recombines and leaves the surface at much lower temperatures than OH formed by water dissociation on oxygen vacancies.

References

U. Diebold, Surf. Sci. Rep. **48**, 53 (2003).

C. L. Pang, R. Lindsay, and G. Thornton, Chem. Soc. Rev. **37**, 2328 (2008).

S. Wendt, P. T. Sprunger, E. Lira, G. K. H. Madsen, Z. Li, J. Ø. Hansen, J. Matthiesen, A. Blekinge-Rasmussen, E. Laegsgaard, B. Hammer, and F. Besenbacher, Science **320**, 1755 (2008).

5:00pm SS-ThA10 Atomic Scale Study of Surface Corrosion and Wet Oxidation of Cu(110) Surface by Water, *B.-Y. Choi*, Lawrence Berkeley National Laboratory, *Y. Shi*, University of California, Berkeley, *M. Salmeron*, Lawrence Berkeley National Laboratory

Dissociated water molecules are at the origin of corrosion and wet oxidation of metals. An atomic scale research is necessary to understand the processes involved in many material industries and the environment science. We investigate the steps leading to corrosion and wet oxidation of Cu(110) surface due to adsorption and dissociation of water molecules using scanning tunneling microscopy. Water is dissociated at 150K and seems to form H2O-OH mixed chain structures along the [110] direction. Growth of a single atomic Cu wire is observed nucleating at the step edges, along with the mixed water chain at high temperature around 180K. The strong bond between hydroxyl molecules and Cu produces the nonvolatile molecule-metal combined structure which is the alternating stripe of them. Further annealing the substrate over 300K dissociates water molecules to leave oxygen atoms on a surface, which form single atomic rows of Cu-O along the [001] direction. This allows us to analyze the inititial steps of wet oxidation of Cu at the atomic scale. The results provide fundamental views of the water related surface chemistry of Cu, with applications to surface engineering of copper-based electrode and catalyst.

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