Wednesday Morning, November 9, 2016

Surface Science
Room 104E - Session SS+AS-WeM

Environmental Interfaces, Ambient Surfaces, and In-Operando Studies

Moderator: R. Scott Smith, Pacific Northwest National Laboratory

8:00am **SS+AS-WeM1 In-situ Electron Microscopy of Synthesis, Chemistry and Self-assembly of Colloidal Nanostructures***, **Eli Sutter**,* University of Nebraska - Lincoln **INVITED**

In-situ microscopy, particularly real-time imaging of dynamic processes has developed into an active field of research and is expected to be one of the key enabling techniques for understanding the formation of nanostructures, catalytic reactions, phase transformations, self-assembly, and other central issues in nanoscience and technology. *In-situ* transmission electron microscopy can be used to follow the behavior and measure the properties of nanostructures over a wide range of environmental conditions with resolution down to the atomic scale. While processes at variable temperatures and gas-solid interactions have been accessible for some time, observations in liquids have emerged only in recent years with the development of special membrane cells. Liquid-cell electron microscopy has developed into a powerful technique that allows the imaging of various processes in wet environments, such as liquids, solutions, or colloidal suspensions, and the investigation not only of a wide range of inorganic nanoscale objects but of biological systems as well.

I will illustrate the power of liquid-cell electron microscopy applied to imaging colloidal synthesis (nanoparticles, core-shell structure), electrochemistry (galvanic replacement reactions) and the self-assembly of nanocrystal superstructures in solution. Our results demonstrate that real-time electron microscopy can substantially advance our understanding of a wide range of processes involving nanoscale objects in bulk liquids.

8:40am **SS+AS-WeM3 Low Energy Electron Microscopy at Near Ambient Pressures***, **Andreas Thissen**,* SPECS Surface Nano Analysis GmbH, Germany

Low-energy electron microscopy (LEEM) is a spectromicroscopy technique, which allows the study of dynamic processes at surfaces and interfaces, such as thin-film growth, surface reactions, and phase transitions. With the FE-LEEM P90 from SPECS, which is based on the instrument design by Rudolf Tromp from IBM [1,2], lateral and energy resolution of below 5 nm and 250 meV, respectively, can be achieved. Depending on the excitation source and the settings on the instrument a variety of different imaging modes are possible: mirror electron microscopy, low energy electron diffraction (LEED), phase contrast imaging, reflectivity contrast, dark field imaging and bright field imaging, as well as photoelectron emission microscopy and spectroscopy.

We have enhanced the technical capabilities of the FE-LEEM P90 towards studies under near ambient conditions by developing a special sample geometry. This enables the analysis of materials and devices under near ambient conditions and even in situ during operation.

9:00am **SS+AS-WeM4 Probing Liquid-Vapor Interfaces of Ionic Solutions with Lab-based APXPS***, **John Newberg**, C. Arble, Y. Khalifa, A. Broderick, S. Rani,* University of Delaware

Ionic interfaces are ubiquitous in physical, chemical, biological, environmental and technological processes. Herein we will present recent efforts examining ionic liquid and deliquescent salt interfaces using lab-based ambient pressure X-ray photoelectron spectroscopy (APXPS) in the presence of water vapor. The onset to water uptake into the top few nm of a hydrophilic ionic liquid is surprisingly similar to hydrophilic solid surfaces. A hydrophilic salt zinc bromide was also probed as it transitions from a solid to a liquid. It will be shown for ionic solutions that the uptake of water leads to variable shifts in the binding energy of anion and cation moieties driven by their interaction with water.

9:20am **SS+AS-WeM5 Effect of Surface Passivation on Stability of Methylammonium Lead Iodide Perovskite***, Q. Peng, **Xiaozhou(Joe) Yu**,* University of Alabama

Methylammonium Lead Iodide Perovskite ($MAPbI_3$) is a promising photoelectronic material for various applications. However, the stability of $MAPbI_3$ is a big concern for its applications in outdoor application environments. Its stability is affected the interfaces between $MAPbI_3$ and other layers of materials, temperature, moisture, and O_2. Currently the detail decomposition mechanism is not clear yet. In this presentation, we will employ a suite of in-situ characterization methods including in-situ Fourier Transform Infrared spectrometer, quartz crystal microbalance, and quadrupole mass spectrometer to understand the decomposition mechanism when expense $MAPbI_3$ to different simulated application environments (such as Fig. 1). The effect of various surface passivation methods on the stability of $MAPbI_3$ will be presented to help illustrate the mechanism that govern the stability of $MAPbI_3$.

9:40am **SS+AS-WeM6 STM Reveals the Formation of Near-Ideal Self Assembled Monolayers on TiO_2 in Air and Solution***, **William DeBenedetti**, M.A. Hines, E.S. Skibinski, A. Song, A. Ortoll-Bloch,* Cornell University

The surface chemistry of TiO_2 in air and solution is an important, but under-studied, topic for next-generation photovoltaics, environmental remediation, and CO_2 photoreduction. Using scanning tunneling microscopy (STM), polarized infrared spectroscopy and other techniques, we will show that surprisingly stable, near-ideal organic monolayers spontaneously form on rutile (110) in a variety of environments.

First, we will show that under ambient conditions, the rutile (110) surface is terminated by a monolayer of bicarbonate, HCO_3, and H formed from the reactive adsorption of CO_2 and H_2O — a reaction that has never been observed in ultrahigh vacuum. Contrary to conventional wisdom, this bicarbonate monolayer displaces H_2O bound to the surface, remaining intact even in vacuum up to ~700 K. The spontaneous formation of a HCO_3 monolayer has important implications for the mechanism of CO_2 photoreduction on TiO_2.

Second, we will show that near-ideal organic monolayers form when rutile (110) is immersed in a variety of aqueous solutions. As an example, highly ordered benzoate monolayers with a characteristic “paired” geometry can be formed from aqueous solutions. Using polarized infrared spectroscopy, we show that this pairing is not due to dimerization, as suggested by previous researchers. Instead, DFT simulations confirm that π-π interactions lead to long-range ordering and a tetrameric bonding geometry. The structure of these monolayers is further confirmed by disrupting the π-π interactions using a variety of fluoro-substituted precursors.

11:00am **SS+AS-WeM10 Study of the Electrical Double Layer of Calcium Carbonate Minerals***, **Yijue Diao**, R.M. Espinosa-Marzal,* University of Illinois at Urbana-Champaign

Understanding the interactions taking place at the calcite-solution interface is crucial to elucidate many natural geochemical processes on or near the Earth’s surface, such as biomineralization and CO_2 sequestration capture of inorganic contaminants by minerals, and enhanced oil recovery. Being the most stable crystalline phase of calcium carbonate, and one of the most abundant minerals, calcite has been studied intensively at the microscale. However, when it comes to the nanoscale, little is known about the molecular details of the calcite-solution interface. Not until recently have experimental and computational works, including our previous force spectroscopy studies, shown that unlike the conventional model of Stern layer, the calcite interface in aqueous phase is well defined by two layers of water molecules on top of which loosely bound hydrated calcium ions are located. Our previous work by colloidal probe atomic force microscopy (AFM) reveals the influence of confinement on the calcite surface under equilibrium conditions.

In this study, AFM with both a microsphere and a sharp tip is employed to perturb the electrical double layer (EDL) of calcite. By performing force measurements with a short interval that does not allow the EDL reaching equilibrium between consecutive force measurements, we perturb the EDL and afterwards scrutinize the kinetics of EDL re-formation. It has been shown that the calcite interface can be tuned by varying calcium concentration and hence, the influence of calcium concentration on the kinetics of EDL formation is also studied. On the other hand, we directly probe into the behavior of the Stern layer by resolving the film thickness transitions (FTTs) that result from squeezing-out layers of molecules confined between the tip and calcite. The significant difference in the confined area, which therefore induces confinements of different extent between the colloidal probe and the sharp tip, allow understanding the influence of the confinement on the EDL.

Calcium carbonate is stored in nanopores of marine organisms and of rocks. Knowing the nanoconfined interfacial structure of calcite from our previous study, we take one step further in this work to investigate the kinetics of the EDL formation under the perturbation induced by consecutive confinement, which allows us not only to spatially elucidate the calcite-solution interface, but also with time resolution.

11:20am **SS+AS-WeM11 Observation of Water Adsorption Structures on Ultrathin ZnO/Au(111)***, **Junseok Lee**, D.C. Sorescu, X. Deng,* National Energy Technology Laboratory

Adsorption of water at the nanostructured metal oxide surfaces has implications in catalysis and serves as a prototypical system in studying water-oxide interfaces. In this work, the adsorption of water on ultrathin ZnO nanostructures grown on Au(111) substrate is investigated using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. Water overlayers are grown on well-defined monolayer and bilayer of ZnO nanostructures. STM images of water overlayer structures on the monolayer and the bilayer of ZnO nanostructures at low temperature are analyzed in detail at different water coverages with the help of DFT calculation results. Moire pattern is found to influence the adsorption structure of water on the ZnO nanostructure surfaces and the brightness of the Moire pattern of the ZnO structure is observed to be significantly modulated by the adsorption of water molecule. Various hydrogen bonded water network structures are observed on ZnO bilayer after desorbing excess water molecules. The edge of the ZnO monolayer is found to be decorated by water molecules up to room temperature but there was no evidence of adsorption of water at the edge of ZnO bilayer.

11:40am **SS+AS-WeM12 Surface and Bulk Crystallization Kinetics of Amorphous Solid Water Nanoscale Films***, **Chunqing Yuan**, R.S. Smith, 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). We directly measure the surface (using TPD) and bulk (using RAIRS) ASW crystallization kinetics as a function of film thickness and temperature. The results show that nucleation and crystallization begins at the ASW/vacuum interface and then the crystallization growth front propagates linearly into the bulk. The linear propagation is further confirmed by adding a thin layer of isotopic D_2O ice indicator at different positions in the ice. These results show that the closer the isotopic layer is to the vacuum interface, the sooner the isotopic layer crystalizes, which confirms the top-down propagation of the crystallization front. Further evidence for ASW/vacuum interface nucleation mechanism comes from experiments where a decane layer is deposited on top of the ASW film. The presence of the decane layer impedes surface nucleation and dramatically decreases the crystallization rate. By separating surface nucleation and bulk propagation processes, we are able to extract the nucleation and growth rates of ASW crystallization between 140-160 K.

This work was supported by the US Department of Energy (DOE), Office of Science, 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.

12:00pm **SS+AS-WeM13 Capture of Hyperthermal Atoms and Molecules by Amorphous Water Ice via Ballistic Embedding***, **Grant Langlois**[*†], S.J. Sibener,* University of Chicago

We present comprehensive work detailing the capture and aggregation of hyperthermal atoms and molecules (CO_2, CF_4, Xe, Kr) by amorphous solid water (ASW) under ultra-high vacuum conditions at 125 K, near the amorphous/crystalline transition. Using time-resolved *in situ* reflection-absorption infrared spectroscopy (RAIRS), the gases prepared in supersonic molecular beams with translational energies above ~3.0 eV are observed to directly embed underneath the vacuum-ice interface to become absorbed within amorphous ice films despite an inability to adsorb at 125 K. Embedding into crystalline films, when observed, is less effective. Upon embedding, resultant mobility within the ice and the strength of intermolecular interactions can yield segregation of these gases into clusters, as seen in the case of CO_2. Tracing the kinetics of these embedding events under different energetic conditions allows for elucidation of the underlying dynamics, and we draw comparison between all studied gases to promote generalized conclusions in regards to empirical prediction of embedding probability. Through application of a classical model of the entrance barrier for atoms and molecules colliding with amorphous ice, we provide direct evidence for a unified connection between embedding probability and momentum of the incoming atoms and molecules; an account of all embedding data measured by our group traces a singular barrier. This work highlights the interplay between translational energy and momentum accommodation during collisions with ice; atoms and molecules can become trapped in an icy surface despite an inability to simply stick to the interface. These results are of considerable importance to studies of both the astrochemistry and evolution of interstellar bodies and dust, and detailing the capture and release of gases by permafrost relating to global climate forcing.

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[*] **Morton S. Traum Award Finalist**

[†] **National Student Award Finalist**

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