

Friday Morning, November 1, 2013

In Situ Spectroscopy and Microscopy Focus Topic

Room: 203 B - Session IS+AS+SP-FrM

Evolving In Situ Microscopic and Spectroscopic Techniques and Applications

Moderator: G. Zhou, Binghamton University

8:20am **IS+AS+SP-FrM1 In Situ Atomic-Scale Observations of the Oxidation of Metals**, G. Zhou, L. Luo, L. Li, State University of New York, Binghamton University, J. Ciston, Lawrence Berkeley National Laboratory, E. Stach, Brookhaven National Laboratory, J. Yang, University of Pittsburgh **INVITED**

Transmission electron microscopy (TEM) has evolved dramatically in recent years and allows for temperature-, time-, and pressure-resolved imaging of gas-surface reactions at the atomic scale. This is accomplished by differentially pumped environmental TEM (max pressures of several Torr) and the incorporation of aberration correction techniques. Here we describe how dynamic, atomic-scale TEM observations of terraces and steps during oxidation of Cu surfaces demands revisions in the current held oxidation mechanism. The canonical description of oxide formation in metals involves a solid-solid transformation proceeding with initial oxygen chemisorption induced reconstructions followed by oxygen subsurface incorporation. Such a mechanism has been inferred from idealized experiments that are primarily restricted to planar surfaces under ultrahigh vacuum conditions. In practice, however, metallic surfaces are seldom perfect. Rather, they contain a high density of low-coordinated surface sites. Thus, in order to gain a detailed understanding of the mechanism of oxide formation under realistic conditions, the role of surface defects during surface oxidation must be elucidated under practical environments. By observing the coordinated step retraction and oxide propagation on surface terraces in real time with in-situ TEM, we demonstrate that the oxide grows via an adatom process, in which Cu atoms detach from step edges and diffuse in along the surface terrace. This process involves neither reconstructive oxygen adsorption nor oxygen subsurface incorporation and is rather different from the mechanism of solid-solid transformation of bulk oxidation that is most commonly postulated. These results demonstrate that the presence of surface steps can promote the development of a flat metal-oxide interface by kinetically suppressing subsurface oxide formation at the metal-oxide interface.

9:00am **IS+AS+SP-FrM3 X-ray Analysis of Ultrastructure of Vitrified Biological Objects**, A.R. Buck, T. Gorniak, T.M. Senkbeil, Karlsruhe Institute of Technology, Germany, V.M. Haramus, Helmholtz-Zentrum Geesthacht, Germany, K. Hilpert, University College London, UK, A. Rosenhahn, Ruhr-Universität Bochum, Germany

Cryogenic sample environments allow investigations in the X-ray 'water window' of 284 – 540 eV which is of tremendous interest for microscopy and coherent scattering due to the high contrast of organic matter with respect to the aqueous background. In addition, no fixatives and stains are required and thus real in-situ analysis becomes possible. We present coherent diffractive imaging and X-ray micrographs of bacteria and compare the data against small angle X-ray scattering on large ensembles. Most measurements have been conducted at the synchrotron BESSY II, U49 PGM2 with our dedicated scattering chamber HORST. As an example for the approach, ultrastructure changes in bacteria induced by stress conditions such as different environmental conditions and biocides. We show that imaging and scattering provide complementary results as latter provides information averaged over thousands of cells and can thus provide insights of a very high statistical quality.

9:20am **IS+AS+SP-FrM4 Recent Advances in the Electrochemical Surface Forces Apparatus**, K. Kristiansen, University of California, Santa Barbara, M. Valtiner, Max Planck Institut für Eisenforschung GmbH, Germany, X. Banquy, Université de Montréal, Canada, G.W. Greene, University of Deakin, Australia, J.N. Israelachvili, University of California, Santa Barbara

We present a newly designed electrochemical Surface Forces Apparatus (EC-SFA) that allow control of surface potential and interfacial electrochemical reactions with simultaneous measurements distances between opposing surfaces (with 0.1 nm resolution), normal interaction forces (with nN resolution), and friction forces (with μ N resolution). We will describe three applications of the EC-SFA:

(1) Oxide growth of a gold surface. Applying a high positive electrical potential on a metal surface will lead to an oxide growth. Using the EC-SFA we compared the measured thickness of the anodic gold oxide layer

and the charge consumed for generating this layer which allowed the identification of its chemical structure as a hydrated Au(OH)₃ phase formed at the gold surface at high positive potentials.

(2) The evolution of the friction forces at a metal-ceramic contact as a function of the applied electrochemical potential.

(3) The phenomenon of "pressure solution". We have found an intimate relationship between dissolution rate and the surface potential difference across interfaces of dissimilar materials that are immersed in brine solution. For example, using the EC-SFA we have visualized and measured the dissolution of silica glass surfaces close to a gold electrode surface, which is on the order of 0.1 nm/hr. This is similar to geological samples of sandstones.

References:

Valtiner M, Banquy X, Kristiansen K, Greene GW, and Israelachvili JN, *Langmuir*, **28** (2012) 13080-13093.

Kristiansen K, Valtiner M, Greene GW, Boles JR, and Israelachvili JN, *Geochimica et Cosmochimica Acta*, **75** (2011) 6882-6892.

Valtiner M, Kristiansen K, Greene GW, and Israelachvili JN, *Advanced Materials*, **23** (2011) 2294-2299.

9:40am **IS+AS+SP-FrM5 Emerging Mesoscale Phenomena in Energy Conversion/Storage Characterized by In Situ Soft X-ray Spectroscopy**, J.-H. Guo, Lawrence Berkeley National Laboratory **INVITED**

Advanced technology arises from the understanding in basic science, and both rest in large on in-situ/operando characterization tools for observing related physical and chemical processes directly at the places where and while reactions occur. In energy science, experimental insight into physical and chemical processes has been largely limited to information obtain with in a framework of thermodynamic and kinetic concepts or atomic and nanoscale. In many important energy systems such as energy conversion, energy storage and catalysis, advanced materials and fundamental phenomena play crucial roles in device performance and functionality due to the complexity of material architecture, chemistry and interactions among constituents within. To understand and ultimately control the interfaces in energy conversion and energy storage application calls for in-situ/operando characterization tools. Soft x-ray spectroscopy may offer some unique features. This presentation reports the development of in-situ reaction cells for soft x-ray spectroscopy towards the studies of photosynthesis and catalytic reactions in recent years. The challenge has been that soft x-rays cannot easily peek into a high-pressure catalytic cell or a liquid photoelectrochemical cell (PEC). The unique design of the in-situ cell has overcome the burden. Some of the instrumentation design and fabrication principle are to be presented, and a number of experimental studies of nanocatalysts are given as the examples, also the recent experiment performed for studying the hole generation in a specifically designed photoelectrochemical cell under operando conditions.

10:20am **IS+AS+SP-FrM7 Changes to the Microstructure of Fibrous Collagen Hydrogels formed under Different Physicochemical Parameters and Upon Cross-Linking with Non-Toxic Reagents are Detected with In Situ Multiphoton Microscopy Imaging**, Y.J. Hwang, X. Lang, J.G. Lyubovitsky, University of California, Riverside

This presentation will highlight the knowledge developed by our laboratory regarding the microstructure of 3D collagen hydrogels detected in situ with multi-photon imaging while employing second harmonic generation (SHG) and two-photon fluorescence (TPF) contrasts. The materials were prepared under different physicochemical parameters and independently stabilized with non toxic cross-linkers. The effects of collagen solid content, incubation temperature and ionic strength as well as cross-linking with genipin and carbodiimide (EDC) on 3D collagen hydrogel microstructure will be addressed. Second Harmonic generation (SHG) contrast was employed to follow modifications and/or evolutions of the hydrogels' microstructure in real time and two-photon fluorescence (TPF) was beneficial in monitoring the extent of the chemical reaction between collagen and genipin as well as spatial locations of the newly induced fluorescent fibers. The induced microstructures differ dramatically upon changing collagen solid content, incubation temperature or ionic strength. For example, short lag time, fast assembly rates and short, tightly connected fibers were detected upon assembly from 30 mM phosphate buffer. In 0.9 M NaCl adjusted 30 mM phosphate buffer only unconnected one micron fiber nuclei with low second harmonic generation contrast formed. Fiber width and length was somewhat similar upon assembly of collagen fibers from 30 mM phosphate buffer adjusted with 0.3 M or 0.6 M NaCl while pore structure depended on the polymerization temperature. Non-zero-length cross-linker genipin induced formation of long aggregated

fluorescent strands throughout hydrogels. The SHG imaging suggested that modification with genipin partially disaggregated initial collagen microstructure within hydrogels at the expense of forming these new fluorescent fibers. On the other hand, zero-length cross-linker EDC, even with an addition of N-Hydroxysuccinimide (NHS), does not affect microstructures. Imaging of the interactions of these important materials with embryonic stem cells induced to differentiate into a neural lineage and implication for tissue engineering will be discussed as well.

10:40am **IS+AS+SP-FrM8 *In Situ* Atomic Scale Observation of Catalyst Surface and Carbon Nanotube Cap Interplay during the Lift-Off.** *M. Picher, P.A. Lin, University of Maryland, College park, J. Winterstein, FEI Co, R. Sharma, National Institute of Standards and Technology*

Catalytic chemical vapor deposition (C-CVD), using a transition metal catalyst (Ni, Fe, Co, etc.) on an SiO₂, Al₂O₃, or MgO support and a carbon-containing precursor (C₂H₂, C₂H₄, CH₄, CO, etc.), is commonly employed for large-scale synthesis of carbon nanotubes (CNTs). However, synthesis of CNTs with the desired structure and morphology for a specific application has still not been demonstrated. Understanding the atomic-scale interplay between catalyst structure and CNT nucleation will aid us in determining the reaction conditions suitable for selective synthesis, especially for single walled CNTs (SWCNTs). During the last decade, the environmental scanning transmission electron microscope (ESTEM) has been successfully employed to reveal the structural, chemical and morphological changes occurring in catalyst nanoparticles during CNT growth. However, the mechanisms of CNT cap formation are yet to be revealed under normal growth conditions: the SWCNT nucleation and growth process is too fast to be captured at currently available video frame rates (30 s⁻¹). We have successfully addressed this problem by slowing the kinetics of the process using a Co-Mo/MgO catalyst system and low pressures of acetylene (C₂H₂) and ethanol (C₂H₅OH) as carbon precursors. Our direct observations show that the CNT cap preferentially nucleates on certain surfaces and first finds two surfaces as suitable anchor points before lift-off. The detailed interplay of catalyst surface structure, cap formation, incubation period, and lift-off will be presented using atomic-resolution videos recorded under these novel CVD conditions. Our observations provide direct insight into the mechanisms of SWCNT growth and open up possibilities for diameter and chirality control.

11:00am **IS+AS+SP-FrM9 *Operando* FTIR-MS Studies of Methanol on WO₃/SBA-15: How Stable Are Methanol Species on Oxide?** *Y. Yang, Pacific Northwest National Laboratory, C. Mims, University of Toronto, Canada, C. Peden, Pacific Northwest National Laboratory, J. Kwak, Ulsan National Institute of Science and Technology, Korea*

Methanol adsorption and desorption are important on many oxide surfaces, for instance, as probe molecules of surface active sites. In this study, atomic layer deposited (ALD) tungsten oxide on silica was used as oxide sample and dimethyl ethylene (DME) synthesis was observed by *operando* FTIR-mass spectroscopy (IR-MS). Methanol adlayer, which contains both methanol and methoxy, was formed by exposing the sample with methanol at low partial pressure (~1 torr) with carrier inert gas at ~1 bar. The stability of the adlayer molecules was observed under two conditions: a) exposed to pure argon purging at different temperatures up to 300 C overnight; b) with constant methanol partial pressure (1 torr) in ambient flow while DME synthesis processed. The kinetics study here requires isotopic deuterated methanol exchange (CD₃OH/CH₃OH). *Operando* IR results shows under condition a), the majority of the adlayer, both methanol and methoxy species, remained on the surface overnight after the highest temperature treatment. Methanol stability is even stronger than methoxy. Temperature dependent IR results show an isosbestic point between the surface water and Methanol species which is direct evidence of water replacement by methanol adsorption. These results further confirms other earlier studies reported. However, under condition b), both replacements transient of surface methanol and methoxy species by deuterated flow are by far much faster. As expected, only CD₃/CH₃ group exchange was observed upon isotope switch in IR and MS results. Measured replacement time constant for Methoxy was ~1000 s and that for methanol was ~2000 s. These surface species transients are compared with simultaneous MS data of gas products with the similar scale of the surface species. These preliminary results indicate that the methanol and methoxy are by far more active on a crowded surface with gas phase methanol exposing comparing a surface with slightly lower coverage and no gas phase exposure. This is a good example of reactivity strong dependence on the surface coverage.

11:20am **IS+AS+SP-FrM10 Coupling Environmental High Resolution Transmission Electronic Microscopy and Raman Spectroscopy: Toward a More Comprehensive *In Situ* Characterization.** *M. Picher, R. Blankenship, S. Mazzucco, R. Sharma, National Institute of Standards and Technology*

In situ imaging, using an environmental scanning transmission electron microscope (ESTEM), has been successfully used to reveal and better understand the crucial chemical and physical processes occurring at the nanoscale, e.g. oxidation/reduction, coalescence, Ostwald ripening, surface reconstruction, substrate/catalyst interaction... However, the relevance of such ETEM studies can be diminished if the following two questions cannot be satisfactorily answered: i) Do high energy electrons affect the reaction mechanism? In other words: is the probed area representative of what is happening on the whole sample? ii) What is the sample temperature in the gaseous environment? Here, we present unique instrumentation that helps to solve these two issues by collecting Raman data during ETEM observation. We can now combine and compare the structural information and kinetics obtained from large (micrometer-scale) areas by the Raman spectrometer with the local information collected by the ETEM at the nanoscale. This system also enables us to simultaneously monitor the actual temperature of the probed material by analyzing shifts in Raman peak frequency. Moreover, this versatile optical setup can be used i) to investigate light/matter interactions (the current 532 nm laser can be easily replaced by any IR/Vis/UV wavelength) ii) as a heating source: the sample can be heated up to 1000°C at 15 mW with a 532 nm laser, iii) for general spectroscopy (absorption, photoluminescence, cathodoluminescence...).

This combined approach is made possible by the insertion of a parabolic mirror in between the sample holder and the lower pole piece of the microscope (Fig1. in Supp Info). It focuses a laser on the sample and collects the scattered Raman photons. A set of optics then carries the Raman signal to the spectrometer.

11:40am **IS+AS+SP-FrM11 New Tools for *In Situ* Chemical and Structural Analysis: Raman and Photoluminescence Go Inside the Vacuum Chamber.** *A.J. King, Renishaw Inc.*

Micro-Raman systems have become very popular tools for analysing novel materials in a wide variety of application areas. Their ease of use has driven them to be employed routinely with carbon materials (graphene, carbon nanotubes, diamond, diamond-like-carbon (DLC)); semiconductors (silicon, germanium, III-V and II-VI materials); photovoltaics (silicon, CIGS, CdTe, CZTS); Chalcogenides (MoS₂, Bi₂Te₃, Bi₂Se₃); as well as oxides, nitrides and carbides. This technology enables researches to probe the molecular structure for phase identification, stress and crystal quality. It can also be used for reaction and catalysis monitoring.

New demands are now being made that require the use of in-situ techniques with very high sensitivity. The ability to conduct measurements inside the vacuum chamber has been enabled with highly efficient optical probes and spectrometer technology to give the required performance in these demanding applications. This talk will cover the basic concepts of Raman spectroscopy, the instrumentation required for these measurements, and highlight some of the applications where in-situ Raman and photoluminescence can increase the understanding of vacuum processes and how they can be optimised to improve quality and yield.

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