

Monday Morning, October 19, 2015

In-Situ Spectroscopy and Microscopy Focus Topic

Room: 211C - Session IS+AS+SS-MoM

Fundamental Studies of Surface Chemistry of Single Crystal and Nanomaterials under Reaction Conditions

Moderator: Franklin (Feng) Tao, University of Kansas, Zili Wu, Oak Ridge National Laboratory

8:20am IS+AS+SS-MoM1 Hot Electron In-Situ Surface Chemistry at Oxide-Metal Interfaces. Foundations of Acid-Base Catalysis, *Gabor Somorjai*, University of California, Berkeley **INVITED**

The development of Catalytic Metal-Semiconductor Nanodiodes (CMSN) to measure the flow of electrons excited during exothermic catalytic reactions at the metal interface proved that oxidation on platinum generates a steady flux of hot electrons [1]. Evidence is presented that the steady state of chemi-current is correlated to the turnover frequency and that the exothermic hot electron production during reactions on transition metal particles may be widespread. The CO/O₂ and H₂/O₂ reactions were studied most frequently by this method and semiconductors included TiO₂, GaN, CoOx, NbOx and TaOx. Charge transport between the metal and oxide interfaces also influences the product distribution of multipath reactions. These were shown in the hydrogenation of furfural and croton aldehyde at platinum/TiO₂ interfaces as compared to the platinum/silica interfaces [2]. The oxide-metal interfaces appear to produce ions, which carry out reactions that have long been called by the organic chemistry community as acid base catalysis. The typical catalytic structure is mesoporous oxide that is produced to hold the metal nanoparticles. The structures produce high surface area oxide metal interfaces and this is a catalytic architecture for acid base catalysis. Studies in changing the transition metal oxide using a single metal of platinum as nanoparticles, shows the tremendous amplification effect of the oxide metal interfaces in the reactions such as the carbon monoxide oxidation. Platinum alone produces on silica three orders of magnitude less CO₂ by the CO oxidation process than on cobalt oxide, that is the most active of these acid base oxide metal interface catalytic systems [3]. Nevertheless, not just cobalt oxide, but nickel oxide, manganese oxide, and iron oxide, produces much higher activity for this reaction than platinum alone. In other reactions, when n-hexane isomerization or cyclisation reactions studied, the pure oxides niobium or tantalum do not produce any reaction other than cracking two smaller molecular fragments. However, at the platinum-oxide interfaces with niobium oxide or tantalum oxide, almost 100% selectivity for isomerization could be achieved [4]. Thus it appears that charge catalysis plays a very important role, which is equal in importance to the role of pure metal covalent catalysis that produces molecules without any apparent charge flow. Generation of hot electron flows and the catalytic activity of two-dimensional arrays of colloidal Pt nanoparticles with different sizes are investigated using catalytic nanodiodes. Pt nanoparticles of smaller size lead to higher chemi-current yield, which is associated with the shorter travel length for the hot electrons, compared with their inelastic mean free path [5]. In many oxide supports microporous sites are used, which are less than 1 nm in size and do not allow the larger platinum nanoparticles inside these pores. In that case, the metal that is used to create the catalysts are deposited on the outside surface of the microporous support. This sort of system, where the metal is outside, but the acidic microporous oxides are inside, can be active only by a spill over of the reaction intermediates from the metal to the oxide - and this is quite well known. However if the micropores are substituted by mesopores in the oxide phase the metal nanoparticles can go inside and then single site oxide-metal interface catalysis commences. These two different catalytic processes, where both the oxide and the metal are catalytically active, deserve attention and distinction.

9:00am IS+AS+SS-MoM3 In-situ GISAXS/GIXAS Characterization of Co_{1-x}Pt_x Bimetallic Clusters under H₂ and CO + H₂ Mixture, *Bing Yang*, Material Science Division, Argonne National Laboratory, *G. Khadra*, *J. Tuaille-Combes*, Institut Lumière Matière, University Lyon & CNRS, France, *E. Tyo*, Material Science Division, Argonne National Laboratory, *S. Seifert*, X-ray Science Division, Argonne National Laboratory, *X. Chen*, Department of Mechanical Engineering, Northwestern University, *V. Dupuis*, Institut Lumière Matière, University Lyon & CNRS, France, *S. Vajda*, Material Science Division, Argonne National Laboratory

CoPt alloy particles have recently attracted great interests for their excellent catalytic and magnetic properties. The alloy phase of cobalt and platinum may create dual-functional sites at the mixed interface which enables novel catalytic properties and synergic effect at nanometer scale. In-situ characterization is thus essential to probe the structure and composition of

bimetallic clusters under reaction conditions in a catalytic process of interest.

Co_{1-x}Pt_x bimetallic clusters with atomic-precise Pt/Co atomic ratio ($x=0, 0.25, 0.5, 0.75, 1$) were synthesized using mass-selected low energy clusters beam deposition (LECBD) technique and soft-landed onto the amorphous alumina thin film prepared by atomic layer deposition (ALD). The median diameter of size-selected Co_{1-x}Pt_x alloy clusters is 3nm with size dispersion lower than 10 % according to transmission electron microscopy (TEM). Utilizing X-ray photoemission spectroscopy (XPS), the oxidation state of as-made clusters as well as the aged particles after extended exposure to air was characterized. After exposure to air, both cobalt and platinum species in the bimetallic clusters are found to be oxidized, while the shift of their covalent state exhibits a non-linear correlation with their atomic composition (Pt/Co).

Utilizing *in-situ* grazing incidence small-angle X-ray scattering and X-ray absorption spectroscopy (GISAXS/GIXAS), the evolution of particle size/shape and the oxidation state of the individual metals are monitored under atmosphere reaction conditions. The as-made Co_{1-x}Pt_x clusters were first pretreated with hydrogen and further exposed to CO and H₂ mixture up to 225°C. The change in the oxidation state of Co and Pt of the supported bimetallic clusters exhibited a non-linear dependency on the Pt/Co atomic ratio. For example, low Pt/Co ratio ($x \leq 0.5$) facilitates the formation of Co(OH)₂, whereas, high Pt/Co ratio ($x=0.75$) stabilizes Co₃O₄ composition instead, due to the formation of Co@Pt core-shell structure where the platinum shell inhibits the reduction of cobalt in the core of the Co_{1-x}Pt_x alloy clusters.

In this work, we have demonstrated *in-situ* measurement of particle size/shape and the oxidation state of supported Co_{1-x}Pt_x bimetallic clusters under operating conditions, and elucidated the different surface structure and chemical state with respect to their atomic ratio. The obtained results indicate ways for optimizing the composition of binary alloy clusters for catalysis.

9:20am IS+AS+SS-MoM4 Novel Surface Oxide on Pt(111) as the Active Phase for NO and CO Oxidation Studied with the ReactorSTM, *Mathijs van Spronsen**, *J.W.M. Frenken*, *I.M.N. Groot*, Leiden University, Netherlands

Platinum finds its main application as a car catalyst to control the emission of exhaust gases. Although automotive catalysis has been extensively investigated, challenges still exist. One of the challenges arises when increasing the oxygen/fuel ratio. Under oxygen-rich reaction conditions, much uncertainty exist about the structure of the active surface phase. This is even true for the Pt(111) surface, which is the facet lowest in energy and the simplest model catalysts available.

An early *operando* Scanning Tunneling Microscopy (STM) study [1] showed a stepwise increase in CO oxidation activity at oxygen-rich conditions. This increase concurred with a dramatic and instantaneous morphology change. From the STM images, the atomic structure could not be resolved, but roughening on a long length scale was observed. Under similar conditions, Surface X-ray Diffraction found the formation of thin, bulk-like α -PtO₂ [2]. Surprisingly, a theoretical study concluded that this oxide is inert to CO oxidation [3].

With the high-pressure, high-temperature ReactorSTM [4], we studied the oxidation of Pt(111) both by exposing to O₂ and to NO oxidation conditions.

Upon oxidation with O₂ (1.0 bar, 423-523 K), we found a stable surface oxide consisting of triangles assembled in a 'spoked-wheel' superstructure. In addition, we found a second structure consisting of a lifted-row pattern. The two structures were coexisting on different regions on the surface. The lifted-row structure was becoming more predominant at higher O₂ pressure. We propose that both oxides share the same building block, which are expanded Pt oxide rows.

After evacuation of the reactor, the ordered structures disappeared, although some remnants remained. The surface oxidation is a clear example of the pressure-gap effect. Furthermore, lower-temperature (291-323 K) experiments did not yield any ordered structure showing the dependence on atomic mobility.

Exposure of Pt(111) to NO and O₂ or exposure to NO₂ resulted in the formation of a mixture of small domains of both the spoked-wheel and the lifted-row structures.

The surface oxidation was accompanied with roughening of terraces. This is attributed to relaxation of adsorbate-induced stress on the surface. Identical roughness development was previously found under CO oxidation

* Morton S. Traum Award Finalist

conditions [1]. Therefore, we argue that a surface oxide was also the relevant structure under CO oxidation conditions.

[1] Bobaru, PhD thesis, Leiden University, 2006

[2] Ackermann, PhD thesis, Leiden University, 2007

[3] Li & Hammer, Chem. Phys. Lett., 409, 1, 2005

[4] Herbschleb, *et al.*, Rev. Sci. Instrum., 85, 083703, 2014

9:40am **IS+AS+SS-MoM5 In Operando Study of Dimethyl Methylphosphonate Degradation Over Metallic and Oxidized Cu(111) Surfaces via Ambient-Pressure X-ray Photoelectron Spectroscopy**, *Lena Trotochaud, A.R. Head*, Lawrence Berkeley National Laboratory (LBNL), *Y. Yu*, University of Maryland, *O. Karslioglu, M. Hartl*, LBNL, *B. Eichhorn*, University of Maryland, *H. Bluhm*, LBNL

Filtration systems for absorption and decomposition of chemical warfare agents (CWAs) are the first line of defense against exposure to these toxic compounds. Composite materials (such as ASZM-TEDA) commonly used in filtration systems consist of high-surface-area carbon supports impregnated with various metals and metal oxides. Despite decades of work to develop highly effective and versatile filtration materials with long-term usability, little is known about the mechanisms of CWA degradation by material surfaces and catalyst deactivation and poisoning, in part due to the challenges involved with spectroscopic characterization of catalyst surfaces under operating conditions. Enabling the rational design of more advanced filtration and decomposition materials for broad-spectrum protection against CWAs and other toxic industrial compounds requires a sophisticated understanding of the chemical mechanisms behind CWA sorption and degradation on the molecular scale.

We will present the surface spectroscopic study of metallic and oxidized Cu(111) single crystal surfaces for catalytic decomposition of dimethyl methylphosphonate (DMMP), a CWA simulant. Ambient-pressure X-ray photoelectron spectroscopy (APXPS) enables examination of these surfaces during DMMP adsorption and decomposition. Initial experiments indicate that adsorption of DMMP on Cu(111) is observed at pressures as low as 1×10^{-7} Torr, and degradation of DMMP is observed at this pressure and higher (60 mTorr) at room temperature. Possible mechanisms of DMMP degradation and deactivation of the surface will also be discussed.

10:00am **IS+AS+SS-MoM6 Bridging the Pressure and Materials Gap between Surface Science and Catalysis: Probing the Surface of Metal Oxide Nanoparticles under Reaction Conditions**, *Maria Kipreos, M. Foster*, University of Massachusetts, Boston

Traditionally, surface science employs ultra-high vacuum, cryogenic conditions and well defined crystal planes; however, heterogeneous catalysis and photocatalysis occur in ambient conditions with complex substrates composed of several crystal planes. Consequently, materials and pressure gaps exist that need to be bridged in order to better understand the surface chemistry of catalysts under reaction conditions. Metal oxide particles employed in catalysis contain a complex matrix of crystal planes, metal/oxygen bonds, metal/hydroxyl bonds, and oxide/water interactions. We utilize *in situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) to monitor reactions from ambient to high pressures between gaseous adsorbates (water, formic acid, and methanol) and metal oxide particles (TiO₂ and ZnO, semiconductors and ZrO₂, an insulator) commonly used as components of catalysts. The internal and external scattering of light that occurs in DRIFTS is well suited for analysis of reactions on the surface of metal oxide nanoparticles. Spectral shifts in frequency, peak area and width values, and absorbance values are used to interpret the structure and reactivity of the surface. Additionally, the use of Confocal Raman Spectroscopy aids in determining the structural variability in these substrates. The use of gaseous probes and these instrumental techniques provides a better understanding of the structure and reactivity of solid nanoparticles surfaces.

10:40am **IS+AS+SS-MoM8 The Use of Integrated Operando, In Situ and DFT Techniques to Unravel the Steps of Heterogeneous Catalytic Reactions**, *Fabio Ribeiro, W.N. Delgass, J. Greeley, R. Gounder, J. Miller*, Purdue University, *W.F. Schneider*, University of Notre Dame

INVITED

Our quest to understand catalysis is limited by our ability to observe the active site while it is turning over. To facilitate this task we developed model catalysts where the active sites are deposited on the external surface area of an appropriate support. Effective characterization, however, happens only with the simultaneous measurement of the rate of reaction while the catalyst is in operation, called operando measurements. The application of operando techniques is becoming a more common tool to help unravel catalytic functions. Our group has custom-built an operando reactor for the measurement of X-ray absorption spectroscopy. While operando measurements are a major improvement, they provide a static picture of a

system that is actually dynamic. Dynamic techniques where the catalyst kinetic and structural properties can be followed simultaneously with a time resolution of a fraction of a turnover are the techniques of choice. We will show examples using a transmission FTIR cell we developed. The great advantage and sometimes necessity of performing experiments in the dynamic and operando modes will be discussed. The help from theory will also be illustrated.

11:20am **IS+AS+SS-MoM10 In Situ XPS Of Graphene-Catalyst Interactions During Chemical Vapor Deposition**, *Robert Weatherup*, Lawrence Berkeley National Laboratory

Critical to controlling the growth of graphene and carbon nanotubes during chemical vapor deposition (CVD) is a detailed understanding of the role of the catalyst, however this remains incomplete due to the wide parameter space. Here we investigate the dynamics of graphene-catalyst interactions during CVD using time- and depth-resolved X-ray photoelectron spectroscopy[1-2], in situ scanning tunneling microscopy,[3] and grand canonical Monte Carlo simulations coupled to a tight-binding model[1]. We focus on Ni(111) as a model catalyst surface and probe in-operando a wide range of hydrocarbon exposure pressures (10^{-6} - 10^{-1} mbar). The key atomistic mechanisms of graphene formation on Ni are thereby revealed and our data highlights an interdependency between the distribution of carbon close to the catalyst surface and the strength of the graphene-catalyst interaction.

The strong interaction of epitaxial graphene with Ni(111) causes a depletion of dissolved carbon close to the catalyst surface, which prevents additional layer formation leading to a self-limiting graphene growth behavior for low exposure pressures (10^{-6} - 10^{-3} mbar). Increasing the hydrocarbon pressure further (to $\sim 10^{-1}$ mbar) leads to weakening of the graphene-Ni(111) interaction accompanied by additional graphene layer formation, mediated by an increased concentration of near-surface dissolved carbon. We also reveal that the growth of more weakly adhered, rotated graphene on Ni(111) is linked to an initially higher level of near-surface carbon compared to the case of epitaxial graphene growth. We relate these results to the simple kinetic growth model that we have previously established,[6] and use them to consistently explain previous graphene CVD results in the literature. The key implications for graphene growth control and their relevance to carbon nanotube growth are thereby highlighted.

References

(1) Weatherup *et al.* J. Am. Chem. Soc. 2014, 136, 13698-13708

(2) Weatherup *et al.* Nano Lett. 2011, 11, 4154-4160

(3) Patera *et al.* ACS Nano 2013, 7, 7901-7912

(4) Weatherup *et al.* ACS Nano 2012, 6, 9996-10003

11:40am **IS+AS+SS-MoM11 Mechanism Study for Salen Ligand Homogeneous Catalyst in a Heterogeneous Catalysis System**, *Niclas Johansson, S. Chaudhary, A.R. Head, O. Snezhkova, J.N. Andersen, J. Knudsen, J. Schnadt*, Lund University, Sweden

Surface-immobilization of transition metal complexes otherwise used as homogeneous catalysts, i.e. in the same (solution) phase as the reactants and products, and their use as heterogeneous catalysts has been an active field of research for many years. The attractiveness of the idea of surface-immobilization lies in the potential to significantly increase the efficiency and selectivity of heterogeneous catalysts [1], the ease of catalyst and product separation [1], and the fact that the need for solvents and highly oxidizing agents might be eliminated in the heterogeneous system.

Here we direct our attention towards the transition metal Mn(III)-salen complex [R,R(-)N,N'-Bis(3,5-di-*t*-butylsalicylidene), 1,2-cyclohexane diaminomanganese(III)chloride] which have been shown to be very effective homogeneous catalysts for enantioselective epoxidation of unfunctionalised olefins. Yet, while much research has been done to investigate the salen complexes' catalytic properties in the homogeneous phase, very few surface science studies have been performed [2,3].

Here we report a study starting from standard UHV conditions and bridging the pressure gap into more realistic conditions. Here, we will show UHV spectra coupled to Torr-range Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS).

We investigated propylene (C₂H₆) epoxidation reaction using surface-deposited Mn(III)-Salen on Au(111) as catalyst. With APXPS we were able to follow the electronic structure changes during reaction conditions in a gas mixture of propylene and oxygen. The spectra acquired show gas phase interactions and changes was found that were specific to the gas mixture. Surprisingly, O 1s spectra acquired at room temperature shows CO₂ which indicates complete oxidation of propylene. This result was further confirmed with a mass spectrometer in direct connection with the reaction chamber. Indeed, the complexes are active even in a heterogeneous system supporting the possibility of transferring homogeneous catalysts into heterogeneous catalytic systems.

References

- [1] C. Copéret and J.-M. Basset, *Adv. Synth. Catal.* 349 , 78 (2007)
- [2] K. Lâmel et al, *Nano Lett.* 10, 2965 (2010)
- [3] A. Schwartz et al., *J. Phys. Chem. C* 117, 1105 (2013)

Monday Afternoon, October 19, 2015

In-Situ Spectroscopy and Microscopy Focus Topic

Room: 211C - Session IS+AS+SA+SS-MoA

Ambient Pressure X-ray Photoelectron Spectroscopy Studies for Catalytic and Energy Materials in Gas Phase

Moderator: Peter Crozier, Arizona State University, Franklin (Feng) Tao, University of Kansas

2:20pm **IS+AS+SA+SS-MoA1 In situ Electron Spectroscopy for Energy Science, Robert Schlögl**, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

The use of volatile renewable electricity in larger amounts in our energy systems requires grid-scale technologies for integration electricity in material energy carrier streams. Several systemic options always suffer from our conceptual weakness to convert free electrons in chemical bonds. This can be achieved with accumulators for limited applications and should be done through water splitting and synthesis of solar fuels in almost unlimited applications. Complex interfacial chemistry is the underlying scientific challenge. To tackle this old challenge with new concepts it is essential to improve our ability to study chemical, electronic and geometric structures of nanoscopic objects in-situ meaning under operation conditions. A whole train of dedicated instrumentation from specimen formation, data acquisition and auxiliary analyses plus sample manipulation is necessary for this task. The presentation gives some aspects of priority challenges and uses examples of operation studies of water splitting catalysts and of CO₂ reduction systems to illustrate the present status of insight. In the outlook the possibilities of the novel experiment EMIL at BESSY will be discussed.

3:00pm **IS+AS+SA+SS-MoA3 Catalysis on Singly Dispersed Bimetallic Sites on Oxide Support, Luan Nguyen**, University of Kansas, A. Frenkel, Yeshiva University, J. Li, Tsinghua University, China, F. Tao, University of Kansas

Reaction events of heterogeneous catalysis occur on specific catalytic sites. Atoms of a catalytic site arrange in a specific geometric/electronic configuration for adsorbing/dissociating reactant molecules and subsequent coupling to form product molecules. Bimetallic catalysts play significant roles in chemical and energy transformations due to their tunable catalytic properties through ligand, geometric, bi-functional, or lattice strain effect.

When a bimetallic site (M_1A_n , M and A: metal elements, $n \geq 1$) is one of the continuous sites on the surface of a bimetallic NP, this site is in a metallic state. However, when M_1A_n sites are *separately* anchored on a surface of a transition metal oxide support, these isolated bimetallic sites are in cationic state. Such change in electronic structure could cause these bimetallic sites to have stronger chemisorption to reactant or/and intermediate molecules, thus facilitating its dissociation and subsequent coupling. In addition, singly dispersion of metal M in M_1A_n minimizes the potential binding configurations of reactant molecules hence may enhance catalytic selectivity toward a specific reaction pathway. Here we present singly dispersed bimetallic catalyst Rh_1Co_3 prepared on Co oxide support, which exhibits 100% selectivity for the production of N₂ in NO reduction with CO.

Preparation of isolated bimetallic sites Rh_1Co_3 on Co_3O_4 nanorods begins with the formation of hydroxide species $Rh(OH)_n$ on the surface of Co_3O_4 , followed by calcination at 150°C in O₂ to form Rh-O-Co bonds between singly dispersed $Rh(OH)_n$ species and the surface of Co_3O_4 , and concluded with a carefully controlled reduction to remove oxygen atoms between Rh and Co and thus a simultaneous formation of Rh-Co bonds. In-situ ambient pressure X-ray photoelectron spectroscopy (AP-XPS) was used to monitor the oxidation and reduction steps and to avoid over or under-reduction.

Formation of singly dispersed Rh atoms was visualized using HAADF-STEM. The bonding environment of Rh to three Co atoms was confirmed using in-situ EXAFS. For reduction of NO with CO, Rh_1Co_3/CoO exhibits high activity at 110 °C with 100% selectivity toward N₂ production. In contrast, Rh-Co alloy NP/CoO has much lower activity and selectivity (10%) under the same condition. In-situ AP-XPS investigation shows that Rh atoms are at cationic state instead of metallic state. Along with this, DFT calculations suggest that a strong adsorption of intermediate N₂O molecules on Rh_1Co_3 site prevents its desorption as a byproduct and provides a dissociation pathway of N₂O to N₂ with a low activation barrier (~0.21 eV), thus leading to a 100% selectivity to N₂ production.

3:20pm **IS+AS+SA+SS-MoA4 Oxidation and Recovery of WC Thin Film Surfaces, E. Monazami**, University of Virginia, J.B. McClimon, University of Pennsylvania, N. Johansson, P. Shayesteh, S. Urpelainen, J. Schnadt, Lund University, Sweden, Petra Reinke, University of Virginia

Transition metal carbide (TMC) surfaces are coveted as catalytic materials, electrodes and hard protective coatings. A bottleneck in their use is surface oxidation, which leads to a decay in performance. Our work establishes the feasibility of surface recovery by using a carbon-rich WC layer where recarbonization of the surface is initiated by an annealing step. Thin carbon-rich tungsten carbide layers are grown by co-deposition of W and C₆₀ on a MgO(001) surface at 1100 K. The MgO substrate serves as a diffusion barrier for carbon, and the films have a well-defined carbon inventory controlled by the deposition rates of the reactants. The film surfaces were studied by in-situ Scanning Tunneling Microscopy and Spectroscopy. Raman spectroscopy confirmed the presence of highly defective graphitic carbon. The oxidation-recarbonization (O-R) cycles were studied in the ambient pressure endstation SPECIES at MAX-Lab (J. Synchr. Rad. 701, 19 (2012)) in a pressure of 0.3 mbar of O₂. Oxidation with $p(O_2)$ of 10⁻⁵ mbar were performed at SPECIES for direct comparison to low $p(O_2)$ STM experiments.

The carbon-rich WC films exhibit a relatively rough surface, which allows only in a few instances true atomic resolution, but graphite as well as graphene layers can be identified. Oxidation at $T > 550$ K leads to etching of surface carbon and the growth of a W-oxide layer and STS maps show the oxide evolution. The oxidation in the low $p(O_2)$ pressure regime progresses slowly and the surface carbide is recovered by annealing.

The use of the SPECIES endstation enabled a quantitative study of the O-R cycles including a detailed analysis of the respective bonding environments which are modified at different times in the O-R cycle. The oxidation in the ambient pressure environment was monitored using the ratio of W-carbide to W-oxide in the W4f core level during the reaction. The steady state thickness of oxide is a function of sample temperature and order of annealing cycles. The surface carbide concentration can be fully recovered in a subsequent annealing step, and repeated O-R cycles were performed. The O-R process is controlled by the interplay between surface oxidation, oxygen and carbon diffusion and our results will be modeled with a simple set of transport equations. We will discuss the role of different bonding environments as we move through the O-R cycle and compare UHV and ambient pressure results up to 800 K. These results clearly illustrate that carbon-rich tungsten carbide materials can be used to achieve a long term use of carbide surfaces in catalysis and fuel cell applications.

supported by NSF-Division of Materials Research (Ceramics) DMR-100580, STINT award.

3:40pm **IS+AS+SA+SS-MoA5 Microscopy, Spectroscopy, and Reactivity of Surfaces in Vacuum and under Ambient Reaction Pressures, Miquel Salmeron, B. Eren**, Lawrence Berkeley National Laboratory **INVITED**

The goal of surface science research is to provide atomic level understanding of the structural and dynamic properties of surfaces, a goal particularly relevant for chemical applications, including catalysis, photochemistry, batteries and fuel cells. With X-ray Photoemission Spectroscopy (XPS) and X-ray absorption Spectroscopy (XAS) we determine composition and electronic structure. With Scanning Tunneling Microscopy (STM) we image atoms and molecules as they adsorb, diffuse and react on single crystal surfaces. To study surfaces in the presence of gases, in the Torr to Atmospheres range, which is relevant to practical catalysis, new instrumentation is needed. Over the last years we developed high pressure STM, XPS and XAS, to study surfaces under high coverage of adsorbates in equilibrium with gases near ambient pressures and temperature. Using a combination of these techniques I will show how under these conditions the structure of surfaces and the adsorbed layers can be very different from that at low coverage, or even at high coverage but at low temperature. Adsorbates can induce dramatic restructuring of the surface, as I will show in the case of CO induced restructuring of Cu surfaces and the reactions with Oxygen.

4:20pm **IS+AS+SA+SS-MoA7 Novel Solutions for Ambient Pressure and In Situ Photoelectron Spectro-Microscopy, Hikmet Sezen, M. Amati, L. Gregoratti**, Elettra-Sincrotrone Trieste, Italy

A technique based on photoelectron spectroscopy (PES) providing simultaneously spectroscopy and microscopy capabilities and being compatible with ambient pressure conditions is still missing. Ambient pressure PES (APPES), based on differential pumping of the electron energy analyzer, offers an optimal spectroscopic solution to overcome

pressure barrier for surface related studies[1]. Unfortunately, APPEs has very limited spatial resolution. On the other hand, a better than 100 nm spatial resolution scanning photoelectron microscope (SPEM), where the X-ray beam is demagnified down to a 130 nm spot by Zone Plate Fresnel optics and the sample scanned under the focused beam, is accessible from a few synchrotrons. A direct adaptation of the APPEs approach to SPEM technique is not possible because of geometric constraints, stabilities and sustainability of the x-ray optics under near ambient pressures, and mechanical stability of the photoelectron detection system under such severe pumping conditions. In this presentation we will introduce two novel solutions for near-ambient pressure SPEM with ~100 nm spatial resolution and compatible with in-situ/operando conditions operated at ESCAmicroscopy beamline at Elettra synchrotron facility.

Dynamic high pressure (DHP) is the one of our near-ambient pressure SPEM solution. The technique is based on generating high pressure pulsed gas packets directed to the sample. Under influence of gas pulses the sample feels a few mbar pressure in a burst instant, then gas packets dilute into the SPEM chamber to yield a 1×10^{-5} mbar background pressure. From the test results a 10^{-3} - 10^{-2} mbar equivalent static pressure was felt by Si and Rh samples during in-situ oxidation reaction.[2] It is available for users.

Effusive cell is another solution for near-ambient pressure SPEM. The sample is encapsulated with a vacuum sealed cell and located just 30-50 μm behind of a 200 μm diameter size pinhole. The focused x-ray beam are scanning the sample through the pinhole. The generated photoelectrons come out from the same pinhole and are able to reach the electron energy analyzer. Due to the geometric orientation of energy analyzer and the pinhole we can achieve ca. a $200 \times 100 \mu\text{m}^2$ aerial point of view on the sample. The pressure inside the cell can be raised up to mbar range while the pressure in the main chamber kept around 1×10^{-5} mbar which is the safety limit for SPEM system. An encapsulated filament is behind the sample for heating, and other electrical connections are ready for biasing of sample, and thermocouple connections.

[1] D. F. Ogletree, et al. Rev. Sci. Instrum. 73, 3872 (2002)

[2] M. Amati, et al. J. Instrum. 8, 05001 (2013)

4:40pm **IS+AS+SA+SS-MoA8 In Situ Studies of Partial Oxidation of Methanol to Hydrogen on Isolated Bimetallic Site Pt_1Zn_n** , Shiran Zhang, L. Nguyen, University of Kansas, A. Frenkel, Yeshiva University, J. Liu, Arizona State University, F. Tao, University of Kansas

Partial oxidation of methanol to hydrogen and carbon dioxide offers a novel route in converting liquid fuel to hydrogen for fuel-cell systems and thus has been widely investigated in the past decade. One important category of heterogeneous catalysts for catalyzing this reaction is bimetallic nanoparticles which consist of continuous bimetallic sites in a metallic state. Isolation of such bimetallic sites through anchoring them on oxide could offer distinctly different catalytic performance in contrast to continuous sites on bimetallic nanoparticles.

Here we reported an isolated bimetallic site Pt_1Zn_n supported on ZnO which offers an extremely high catalytic activity with high selectivity for transformation of methanol to hydrogen with oxygen. It was prepared through a restructuring of singly dispersed Pt atoms on ZnO with reducing treatment. The formed isolated Pt atoms on ZnO was characterized with high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) along the projected [10-10] of ZnO as well as the corresponding structural model (Figure 1). The bright spots show single dispersion of Pt atoms. The offset of Pt atoms to the Zn atom row suggests Pt atoms are on the column of oxygen atoms, which indicates the bonding of Pt atom to Zn atoms. Photoemission features of Pt4f of the catalyst during catalysis were tracked with ambient pressure X-ray photoelectron spectroscopy (AP-XPS) using monochromated Al K α (Figures 2). The resultant partial reduced state of Pt atoms under reaction conditions is consistent with the electronic state of Pt in Pt_1Zn_n bimetallic site.

Catalytic performance of the formed isolated Pt_1Zn_n bimetallic site in partial oxidation of methanol was evaluated and compared with Pt-Zn bimetallic nanoparticle catalyst (Figure 3). Isolated Pt_1Zn_n bimetallic site catalyst exhibits much higher activity per active site and selectivity to H_2 than Pt-Zn nanoparticle catalyst in transformation of methanol to hydrogen through partial oxidation. The cationic nature of these isolated bimetallic site in contrast to the metallic nature of active sites on a nanoparticle could be responsible for the differences in catalytic performance. This study illustrates that isolation of continuous bimetallic sites on a nonmetallic support is a new opportunity to tune catalytic performance of bimetallic catalysts.

5:00pm **IS+AS+SA+SS-MoA9 New Developments in Small Spot and Imaging Near Ambient Pressure XPS**, Andreas Thissen, SPECS Surface Nano Analysis GmbH

Over the last 15 years, Near Ambient Pressure (NAP-) XPS has demonstrated its promising potential in a wide variety of applications. Starting from the Catalysis and Ice paradigm, the focus has shifted towards solid-liquid interfaces, liquid jets and in-situ electrochemistry. Initially, the experiments had to be carried out using advanced synchrotron sources to reach reasonable count rates. But now, the SPECS PHOIBOS 150 NAP offers optimized transmission for electrons, even at pressures up to and above 100mbar, so researchers can now use it with conventional X-ray and UV sources in their own laboratories. Because of the widened application fields, standard XPS is now also attainable when combined with easily adjustable monochromated X-ray sources that offer stable operation, small excitation spots, and high photon flux densities, even in Near Ambient Pressure conditions. The latest designs and results are presented showing small spot performance for spot sizes < 30 μm , while also showcasing the latest implementations of imaging NAP-XPS that uses a new concept allowing for lateral resolved measurements without a compromise in count rate and usability. Highlighting on how sample environments (in situ cells for gases and liquids, electrochemical cells, gas inlets) and integration are both absolutely essential to obtain relevant results from well-defined samples, the presentation will demonstrate the use of NAP-XPS systems for high throughput-XPS measurements, as well as a variety of applications.

5:20pm **IS+AS+SA+SS-MoA10 In Situ Measurement of the Abundances and Temperatures of the Constituents of Semiconductor Manufacturing Plasmas via Terahertz Absorption Spectroscopy: Comparison with Theoretical Models**, Yaser Helal, C.F. Neese, F.C. De Lucia, The Ohio State University, A. Agarwal, B. Craver, P.R. Ewing, P.J. Stout, M.D. Armacost, Applied Materials, Inc.

Plasmas used by the semiconductor manufacturing industry are similar in pressure, temperature, and electron density to those used for the laboratory study of astrophysical neutrals, ions, and radicals. Thus, methods developed over several decades in the submillimeter/terahertz spectral region are directly applicable. Important attributes of terahertz absorption spectroscopy are that it can provide from first principles, without need for calibration, absolute concentrations and temperatures. Furthermore, since there are no intrusive probes, terahertz observations do not impact or change the plasma under study. Such measurements provide details and insight into the interactions and reactions occurring within the plasma and their implications for semiconductor manufacturing processes. In this work, a continuous wave, 0.5 – 0.75 THz absorption spectrometer was developed and used to study the processes in a commercial inductively coupled plasma (ICP) etch chamber. Because of the relatively long wavelength of the terahertz radiation, diffraction is more serious than in the optical regime. As a result, an important part of this work was the development of optical strategies to couple this spectrometer to the plasma reactor using its existing viewports. Comparisons of the experimental results with predictions from equipment models for ICPs will also be presented for Ar/CF $_4$ /CHF $_3$ with varying pressures, powers, and gas mixture ratios. Comparisons such as this provide a basis for validating and improving models, whose development is a complex and difficult science in itself. The results presented in this talk show that terahertz rotational spectroscopy can provide unique and easy to interpret information about manufacturing plasmas and is a useful development tool for process, theoretical and physical models, and the improvement of etch methods.

In-Situ Spectroscopy and Microscopy Focus Topic

Room: 211C - Session IS+AS+SA+SS-TuM

In-situ Studies of Solid-liquid Interfaces

Moderator: Anatoly Frenkel, Yeshiva University, Franklin (Feng) Tao, University of Kansas

8:20am **IS+AS+SA+SS-TuM2 Water at Ionic Liquid Interfaces Probed by APXPS, John Newberg, Y. Khalifa, A. Broderick, University of Delaware**

Ionic liquids (ILs) have a wide array of applications in biotechnology, coatings, synthesis, separations, and energy sciences. Many of these processes involve either IL-solid or IL-vapor interactions. It is therefore critical we understand the fundamental interfacial properties of ILs on a molecular level. Due to the ubiquity of water, its influence on the properties of ILs has been the focus of many bulk studies and, more recently, surface science studies. Here we will highlight the use of a recently commissioned ambient pressure X-ray photoelectron spectroscopy setup in our laboratory and its application in characterizing the interfacial region of hydrophilic and hydrophobic ILs upon interaction with water vapor as a function of increasing pressure.

8:40am **IS+AS+SA+SS-TuM3 Probing the Liquid-Solid Interface of polycrystalline Pt in 1.0 M KOH using Ambient Pressure Photoemission Spectroscopy and "Tender" X-rays, Marco Favaro, B. Jeon, P.N. Ross, Z. Hussain, J. Yano, Z. Liu, E.J. Crumlin, Lawrence Berkeley National Laboratory (LBNL)**

With the previous success in soft X-ray AP-XPS gas-solid interface^{1a-e} probing, researchers have started to gain insights into the liquid-solid boundaries^{1d}. Taking the cue from these new research frontiers, we have developed on BL 9.3.1 at the Advanced Light Source (LBNL) a new liquid phase AP-XPS system (based on a Scienta R4000 HiPP-2 analyzer) that will shed new light on the understanding of the chemical changes at the electrode surfaces during normal working conditions, leading to a great enhancement of our knowledge on the most important processes in energy conversion and storage^{2a,b}. The combination of this new system with synchrotron radiation in the "tender" X-ray region (between 2 and 7 keV), allows us to probe the interface between thin liquid and solid phases using high kinetic energy photons and then, thanks to the *in operando* approach, directly track the phenomena occurring at the electrode liquid-solid interface during the electrochemical reactions of interest. The technique developed at BL 9.3.1 allows the study of both gas-liquid and liquid-solid interfaces, for pressures up to a hundred of Torr^{2a}.

In order to deeply investigate the possibilities offered by this new technique and, at the same time, to establish a benchmark, a reference material such as polycrystalline Pt has been studied in 1.0 M KOH electrolyte. In this talk we will demonstrate that it is possible to have fine control of the applied potential^{2a,b}, measuring the core level binding energy shift of the oxygen 1s and potassium 2p photoemission lines, according to the applied external potential. Moreover we will discuss the observation, under *in operando* conditions, of the changes of the surface oxidation state^{2b} of Pt triggered by the applied potential. Thanks to the innovative experimental approach, we have observed the *in situ* formation of Pt(II) and Pt(IV) species during the oxygen evolution reaction (OER), as well as the reversibility of the surface chemistry passing from anodic to cathodic potentials (up to the hydrogen evolution reaction, HER).

[1] a. Lu et al., *Sci. Rep.* **2**, 715 (2012); b. Zhang et al., *Nat. Mat.* **9**, 944 (2010); c. Axnanda et al., *Nano Lett.* **13**, 6176 (2013); d. Starr et al., *Chem. Soc. Rev.* **42**, 5833 (2013); e. Mudiyansele et al., *Angew. Chem. Int. Ed.* **52**, 5101 (2013).

[2] a. S. Axnanda, E. Crumlin et al., *Sci. Rep.*, accepted; b. E. Crumlin et al., *in preparation*.

9:00am **IS+AS+SA+SS-TuM4 Toward Ambient Pressure Electron Spectroscopy with Conventional XPS Instrumentation, Andrei Kolmakov, National Institute of Standards and Technology (NIST)**

The current state of the art instrumentation for ambient pressure electron spectroscopy requires highly specialized sophisticated laboratory equipment or dedicated synchrotron radiation facilities. The limited access to these equipment impedes *in situ* (*in vivo*) studies under realistic conditions in catalysis, energy, environmental and bio-(medical) fields. We propose a new sample platform which enables ambient pressure XPS to be conducted using conventional XPS instrumentation. The core of the sample platform is

microchannel environmental cells sealed with electron transparent, molecularly impermeable, mechanically and chemically stable graphene layer. The channels can be impregnated with liquids or gases and yet be vacuum compatible. Two major wafer scale fabrication strategies: (i) transferred graphene and (ii) as grown graphene layer were described. The coverage yield, membrane cleanness and leaking rates were comparatively studied. The feasibility tests of the platform included *in situ* XPS and electron microscopy studies of the water radiolysis and electrochemical processes taking place at liquid electrolyte-solid interface.

9:20am **IS+AS+SA+SS-TuM5 Solvation and Chemistry at the Interface: Near Ambient Pressure Electron Spectroscopy Studies of Aqueous Solution Interfaces, John Hemminger, University of California, Irvine**

INVITED
We have combined liquid-jet photoelectron spectroscopy coupled with classical molecular dynamics simulations to study the composition and chemistry of the liquid/vapor interface of aqueous solutions. Our experiments take advantage of the variable x-ray energy capability of synchrotron radiation and the kinetic energy dependence of the electron inelastic mean free path to carry out experiments with different probe depths. At low x-ray energy the low energy photoelectrons are detected primarily from the surface region of the solution. At higher x-ray energy our experiments probe more deeply into the solution. This allows us to directly compare the liquid/vapor interface with the bulk of the aqueous solution. We will present recent results on aqueous solutions of organonitrile compounds (acetonitrile and propionitrile). Our experiments and MD simulations show that both acetonitrile and propionitrile accumulate at the liquid/vapor interface—even though both nitriles are fully miscible with water. We have also studied the salting in and salting out effects for nitriles in water. We also have studied the effect of ion size on the surface propensity of cations in alkali halide aqueous solutions.

11:00am **IS+AS+SA+SS-TuM10 In situ Single-molecule Microscopy of Photoelectrocatalysis for Solar Water Oxidation, Peng Chen, Cornell University**

INVITED
This talk will present our recent results in using single-molecule super-resolution fluorescence microscopy to image photoelectrochemical reactions on single semiconductor nanostructures *in situ* under photoelectrochemical water oxidation conditions. We separately image hole and electron induced reactions, driven by light and electrochemical potential, and map the reactions at single reaction temporal resolution and nanometer spatial resolution. We also correlate the surface hole and electron reactivity with the local water oxidation efficiency using sub-particle level photocurrent measurements. By depositing oxygen evolution catalysts in a spatially controlled manner, we further identify the optimal sites for catalyst deposition for photocurrent enhancement and onset potential reduction.

11:40am **IS+AS+SA+SS-TuM12 In Situ and Operando AP-XPS for the Oxidation State of Pd at Solid/Liquid Interface, Beomgyun Jeong, M. Favaro, P.N. Ross, Z. Hussain, Lawrence Berkeley National Laboratory (LBNL), Z. Liu, Shanghai Institute of Microsystem and Information Technology, China, B.S. Mun, J. Lee, Gwangju Institute of Science and Technology, Republic of Korea, E.J. Crumlin, Lawrence Berkeley National Laboratory (LBNL)**

A catalyst is defined as a substance that enhances a reaction rate without changing its chemical state. However, often the chemical state of a catalyst surface undergoes changes during the reaction, leading to the degradation of catalyst performance. These phenomena are particularly significant in electrocatalysis in which reaction occurs at solid/liquid interface with electrical potential as an activation energy to drive the reaction. In order to understand the mechanism of catalyst degradation, it is important to have a capability to observe the chemical states of electrode and various chemical species in electrolyte during the reaction taking place at the solid/liquid interface. In order to explore this region, we have developed a new experimental approach [1], using ambient pressure XPS (AP-XPS) coupled with "tender" X-rays (in the range between 2.5 and 7.0 keV) at the Advanced Light Source BL 9.3.1, Lawrence Berkeley National Laboratory. Because of the relatively high kinetic energy of the incoming photons, "tender" X-rays allow probing solid/liquid interfaces through thin electrolyte films characterized by a thickness of 10-30 nm. This unique functionality allows the ability to simultaneously correlate the electrocatalytic activity of electrodes to both the chemical modifications of the electrode surface, and the electrolyte.

This talk will provide details on *in-situ* and *operando* AP-XPS measurements on the chemical modifications of polycrystalline Pd surface studied at different electrochemical potentials. Pd is a cost-effective materials alternative to Pt showing similar electrocatalytic property of Pt in

various reactions, such as oxygen reduction and electrooxidation of hydrogen and formic acid. On the other hand, it is well known that the Pd activity decreases faster than that of Pt especially in formic acid oxidation [2]. This phenomenology could be understood by the direct observation of the Pd surface chemistry evolution at electrified solid/liquid interface. We will discuss the performance of the Pd electrode in two different aqueous electrolytes, in particular in an alkaline medium and in a formic acid solution, an electroactive liquid organic molecule. We believe that our findings represent a step forward in the rationalization of the electrocatalytic behavior of Pd.

[1] S. Axnanda, E.J. Crumlin *et al.*, *Sci. Rep.* 5 (2015) 9788.; b. E.J. Crumlin *et al.*, in preparation.

[2] H. Jeon, S. Uhm, B. Jeong, J. Lee, *Phys. Chem. Chem. Phys.* 13 (2011) 6192.

12:00pm **IS+AS+SA+SS-TuM13 In situ Characterization of Switchable Ionic Liquids by Liquid ToF-SIMS and SALVi**, *Juan Yao, X. Sui, D. Lao, Y. Zhou, S. Nune, D. Heldebrant, Z. Zhu, X.-Y. Yu*, Pacific Northwest National Laboratory

A vacuum compatible microfluidic reactor, SALVI (System for Analysis at the Liquid Vacuum Interface) was employed for *in situ* chemical imaging of switchable ionic liquids (SWILs) using time-of-flight secondary ion mass spectrometry (ToF-SIMS). A model SWIL system consisting of 1,8-diazabicycloundec-7-ene (DBU) and 1-hexanol with CO₂ gas to change solvent polarity was selected. A series of ionic liquids with different CO₂ loading was analyzed. Spatial chemical differences were observed within the same ionic liquid, indicating inhomogeneity of the ionic liquid. Spectral principal component analysis (PCA) was conducted using both positive and negative ToF-SIMS data. Clear distinctions were observed among SWILs of different CO₂ loadings. The loading plots strongly indicate that fully loaded SWILs share similar spectral components as those of the non-loaded ILs. This finding confirms the hypothesis of the biphasic structure in the fully loaded IL predicated by molecular dynamic simulation and presents the first physical evidence of the liquid microenvironment of IL determined by liquid ToF-SIMS. Various ion pairs were also observed in addition to the known SWIL chemistry of the DBU and 1-hexanol system, indicating the complexity of the ionic liquid previously unknown. The vacuum compatible microchannel in SALVI provides a new way to study ionic liquids in vacuum by sensitive surface techniques. Our approach directly visualized spatial and chemical heterogeneity within the SWILs by dynamic liquid ToF-SIMS for the first time.

Tuesday Afternoon, October 20, 2015

In-Situ Spectroscopy and Microscopy Focus Topic

Room: 211C - Session IS+AS+SS-TuA

Environmental TEM Studies for Catalytic and Energy Materials

Moderator: Franklin (Feng) Tao, University of Kansas, Judith Yang, University of Pittsburgh

2:20pm **IS+AS+SS-TuA1 In Situ and Operando TEM of Thermal and Photocatalysts**, Peter Crozier, B.K. Miller, L. Zhang, Q. Liu, Arizona State University **INVITED**

Heterogeneous catalysts play a vital role in the development of energy technologies. Understanding the fundamental relationships between catalyst activity and structure at the nanoscale will enable the improved design of catalyst nanostructures. *In-situ* and *operando* environmental transmission electron microscopy (ETEM) is a powerful technique for the investigation of structure-reactivity relationships in high surface area catalysts under reaction conditions. With current instruments, atomic resolution imaging and spectroscopy can be carried out in the presence of gas, liquid, light and thermal stimuli. The combination of mass spectrometry and electron energy-loss spectroscopy allow catalytic products to be detected and quantified directly in the electron microscope. Several specific applications of ETEM instrumentation and experiments to several heterogeneous catalysts will be presented.

Photocatalytic water splitting can be accomplished by a heterostructure of several materials, including a light absorbing semiconductor and one or more co-catalysts. Our group has focused on Ni-NiO co-catalysts on both TiO₂ and Ta₂O₅. In the Ni-NiO/TiO₂ system, deactivation occurs due to this Ni dissolution into water during illumination and H₂ is only produced by the oxidation of Ni metal[1]. For the Ta₂O₅ supported catalyst, H₂ was produced predominantly by a catalytic reaction [2] and the deactivation rate was found to be inversely proportional to the initial thickness of the NiO shell. In both systems, deactivation is observed only during light illumination, so that this deactivation is properly called photocorrosion.

Our group has also been pioneering the use of operando TEM to study CO oxidation over supported Ru nanoparticles [3]. There is uncertainty and debate in the literature regarding the most active form of this catalyst. Images of the Ru nanoparticles after reduction *in-situ* show a clean metal surface, but after only 0.5% O₂ is introduced into the cell, a thin oxide layer forms on the surface. Similar experiments are currently being performed under operando conditions.

References:

- [1] L. Zhang, et al. The Journal of Physical Chemistry C, **119**, (2015), p. 7207–7214.
- [2] Q. Liu, et al. Applied Catalysis B: Environmental, **172–173**, (2015), p. 58–64.
- [3] B.K. Miller, P.A. Crozier Microscopy and Microanalysis **20**, (2014), p. 815–824.
- [4] The support from the U.S. Department of Energy (DESC0004954), and the National Science Foundation (CBET-1134464), and the use of ETEM at John M. Cowley Center for HR Microscopy at Arizona State University is gratefully acknowledged.

3:00pm **IS+AS+SS-TuA3 Environmental TEM Study of Gold and Platinum Nanoparticulate Catalysts**, H. Yoshida, Y. Kuwauchi, H. Omote, Seiji Takeda, Osaka University, Japan **INVITED**

The catalytic activity of metal nanoparticles depends on their size, shape, and surface structure. It is well-known that the adsorption of gases induces changes in the shape and surface structure of metal nanoparticles. Thus, it is important to obtain structural information about metal nanoparticles under reaction conditions to elucidate the correlation between the catalytic activity and the morphology of the nanoparticles. Environmental transmission electron microscopy (ETEM) is one of the powerful methods for the study of catalytic materials under reaction conditions at atomic scale [1]. In this study, we have investigated the shape and surface structure of Au and Pt nanoparticles that are supported on CeO₂ in reactant gases by a Cs-corrected ETEM.

We have found that the surface structure of a Au nanoparticle was reconstructed during CO oxidation at room temperature [2]. The {100} facets remain unreconstructed in vacuum. Under CO oxidation reaction conditions, the Au atomic columns on the topmost and second topmost {100} layers shift to peculiar positions. In the reconstructed surface the Au

atoms on the topmost surface layer form an undulating hexagonal lattice, while those on the second topmost surface layer form a normal square lattice with slight distortion. This atomic-scale *in-situ* visualizing method provides us with insights into reaction mechanisms in heterogeneous catalysis.

We have observed the oxidation and reduction processes of the surface of Pt nanoparticles by ETEM. Atomic layers of Pt oxide were formed gradually in O₂ at room temperature during ETEM observations. In situ atomic resolution ETEM, combined with in situ electron energy-loss spectroscopy, showed that atomic layers of Pt oxides, including α -PtO₂ and Pt oxides of other forms, first started forming on the preferential facets of Pt nanoparticles at the early stage, entire oxidization on the whole surface of Pt nanoparticles then followed. The oxides were reduced promptly to Pt by adding a small amount of CO or H₂O vapor to the dominant O₂ gas. It is concluded that electron irradiation during ETEM observation activates the gases non-thermally, therefore promoting or suppressing the processes at room temperature [3].

[1] S. Takeda, Y. Kuwauchi, H. Yoshida, *Ultramicroscopy*, **151** (2015) 178.

[2] H. Yoshida, Y. Kuwauchi, J. R. Jinschek, K. Sun, S. Tanaka, M. Kohyama, S. Shimada, M. Haruta, S. Takeda, *Science***335** (2012) 317.

[3] H. Yoshida, H. Omote, S. Takeda, *Nanoscale*, **6** (2014) 13113.

4:40pm **IS+AS+SS-TuA8 Environmental Study of the Reaction-driven Restructuring of Ni-Co Bimetallic Nanoparticles**, C.S. Bonifacio, University of Pittsburgh, H.L. Xin, Brookhaven National Laboratory, Sophie Carenco, M.B. Salmeron, Lawrence Berkeley National Laboratory, E. Stach, Brookhaven National Laboratory, J.C. Yang, University of Pittsburgh

Bimetallic nanoparticles (NPs) possess novel catalytic, optical, and electronic properties compared to their monometallic counterparts. These catalytic properties can be controlled by fine-tuning the NP structure and dimension, surface oxidation, and chemical composition. For instance, bimetallic NPs with a core-shell structure can allow for fine tuning of reactivity, averting sintering issues in the core, and even increase tolerance to high temperature exposure. Above all, elemental segregation in the core-shell structure has been demonstrated as a potential route of modifying the NPs catalytic properties through *in situ* gas reaction studies. To confirm this hypothesis, we have used *in situ* imaging and spectroscopy techniques to study Ni-Co core-shell NPs under environmental conditions to provide direct evidence of elemental redistribution during reaction. Two pairs of oxidation and reduction reactions were performed in an environmental transmission electron microscope (ETEM) at 0.3 Torr in O₂ and H₂ gas at 220°C and 270°C, respectively. Electron diffraction patterns and electron energy loss spectroscopy (EELS) maps showed a reaction-driven restructuring of the core-shell NPs with Ni species migrating to the NP surface by the 2nd reduction cycle. These results are in agreement with previous ambient-pressure x-ray photoelectron spectroscopy (AP-XPS) studies of the same NPs under identical reaction conditions. Furthermore, the ETEM results confirm the NP structure without erroneous interpretations that may result from post-mortem analysis of the samples. Quantitative analysis of the EELS results is underway to identify the valence states during the oxidation-reduction reactions. Correlation of the reaction-driven restructuring of NPs with the electronic structure changes from ETEM and AP-XPS will provide insight into the optimum reaction conditions, i.e., catalytic properties, of the Ni-Co core-shell NPs in challenging reactions such as selective CO₂ reduction.

5:00pm **IS+AS+SS-TuA9 In situ Vibrational Spectroscopy Investigation of the Surface Dependent Redox and Acid-base Properties of Ceria Nanocrystals**, Zili Wu, Oak Ridge National Laboratory **INVITED**

Ceria is best known for its excellent redox property that makes it an important component in the three-way catalyst for auto exhaust cleanup. This is a result of its high oxygen storage capacity associated with the rich oxygen vacancy and low redox potential between Ce³⁺ and Ce⁴⁺ cations. Equally interesting yet less is known about ceria is its versatile acid-base properties. Either as a standalone catalyst, a modifier or a support, ceria and ceria-based catalysts can catalyze the transformation of a variety of organic molecules that makes use of the acid-base as well as the redox properties of ceria.

Recent advances in nanomaterials synthesis make it possible to achieve nanocrystals with crystallographically defined surface facets and high surface area, which can be considered as ideal model systems for catalytic studies under realistic conditions. In this work, I will showcase how we can make use of ceria nanoshapes as model systems to gain molecular level understanding of the shape effect on both redox and acid-base properties

and catalysis of ceria nanocrystals *via in situ* IR and Raman spectroscopy. Insights have been gained into how the surface structure of ceria catalyst affects profoundly its redox and acid-base properties and consequently the catalytic behaviors. It is suggested that the surface structure of ceria controls the catalytic performance through the combination of various factors including structure-dependent surface sites geometry, lattice oxygen reactivity, surface vacancy formation energy, defect sites, and acid-base property on ceria.

Acknowledgements: This work was supported by Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy. A portion of the work was supported by the Center for Understanding & Control of Acid Gas-Induced Evolution of Materials for Energy (UNCAGE-ME), an Energy Frontier Research Center funded by DOE, Office of Science, Basic Energy Sciences. The IR and Raman work were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

5:40pm **IS+AS+SS-TuA11 Direct Writing of sub-10 nm Structures from Liquid with Helium Ions.** *V. Iberi, R.R. Unocic, Nathan Phillip, A. Belianinov, A.J. Rondinone, D.C. Joy, O.S. Ovchinnikova,* Oak Ridge National Laboratory

In-situ direct writing by electron beam from solutions opens a pathway for resistless fabrication of nanostructures at high throughput. However, when using electrons to direct write in solution the minimal size of the created structures is limited to the micron scale due to fundamental physics of the interactions between the electron beam and the liquid, including the lateral transport of solvated electrons and ionic species. Use of the helium beam with the opposite charge and shorter mean free path offers the potential for the localization of the reaction zone on the single digit nanometer scale. Here we will present our results demonstrating writing of platinum structures from liquid (beam induced electroplating) in a platinum chloride solution using helium ions with sub-10 nm resolution. Using data analytics on acquired in-situ growth movies we are able to elucidate the main statistical descriptors for helium ion beam initiated platinum structure growth. The possible mechanisms of beam induced growth and ultrahigh localization of reaction zone are discussed. Furthermore, we will discuss optimization of solution chemistry and instrumental parameters as they relate to the quality and thickness of structures and the extension to device fabrication on a single digit nanometer level.

This work was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy (DOE) Office of Science User Facility.

Tuesday Evening Poster Sessions

In-Situ Spectroscopy and Microscopy Focus Topic

Room: Hall 3 - Session IS-TuP

In-Situ Spectroscopy and Microscopy Poster Session

IS-TuP1 Investigations of Graphene Covered Metal Catalyst using Operando Ambient Pressure X-ray Photoelectron Spectroscopy. *Qiang Liu*, Lawrence Berkeley National Laboratory (LBNL), *B.H. Mao*, Chinese Academy of Sciences, *E.J. Crumlin*, Lawrence Berkeley National Laboratory (LBNL), *Z. Liu*, Chinese Academy of Science

Carbonaceous deposition is always observed in carbon-containing catalysis reactions on metal catalysts. This carbon deposition layer blocks the active sites of the metal catalyst and, therefore, inhibits the catalytic reaction. Recent research revealed that by depositing a graphene overlayer on metal catalyst the detrimental interaction between reactant gases and the metal catalysts can be weakened, thus resulting in a lowering of the activation energy barrier for the desired catalytic reaction. In order to probe the fundamental charge transfer processes between the as-grown graphene layer and the metal catalyst we present our studies of this system using operando ambient pressure X-ray Photoelectron Spectroscopy (APXPS), with synchrotron X-rays at the Advanced Light Source, Lawrence Berkeley National Laboratory. By intercalating gases (e.g. CO, O₂) quasi-free-standing graphene can be prepared, which annulled the charge transfer between as the as-grown graphene and the metal. Using APXPS, we have studied the graphene-reactant and reactant-metal interactions under different temperature and pressure conditions. We will discuss the results from graphene-Cu and graphene-CuNi system under CO oxidation reaction and other reaction conditions.

IS-TuP2 Probing the Electrode-Electrolyte Interfaces using In Situ Angle-resolved XPS. *V. Shutthanandan*, *M.I. Nandasiri*, *A. Schwarz*, *T.C. Kaspar*, Pacific Northwest National Laboratory, *S.A. Thevuthasan*, Qatar Environment and Energy Research Institute, Qatar, *Murugesan Vijayakumar*, Pacific Northwest National Laboratory

The interaction between a charged surface (i.e. electrode) and an ionic solution (i.e. electrolyte) is the basic science that drives various systems ranging from biological membranes to energy storage and conversion devices. In a typical electrode-electrolyte interfacial region, ions from the electrolyte can form an electric-dipole with oppositely charged electrode and subsequently produce an electric double layer (EDL). This EDL formation is a highly reversible process that involves no chemical/phase changes and is widely used in modern devices such as chemical sensors, field-effect transistors and supercapacitors. However, a clear understating of the impact of the electrode surface chemistry and the nature of electrolyte ions on molecular structure-property relationship at modern interfaces is still lacking. One of the unique features of these interfaces is that they contain non-equilibrium ion concentration under biased conditions. A multilayer formation with alternative charges (i.e., cation/anion) is expected under charged conditions, which can subsequently result in gradient change in ion concentration depend on the applied potential. To clearly distinguish the role of each electrode/electrolyte parameter under charging conditions, an unique *in-situ* angle-resolved X-ray photoelectron spectroscopy (AR-XPS) setup was developed at the Environmental Molecular Sciences Laboratory (EMSL) in Pacific Northwest National Laboratory. The change in composition of Ionic liquid electrolyte and specifically cation/anion ratio at different charging conditions was analyzed as a function of depth using *in-situ* AR-XPS. Preliminary results obtained from a model system consisted of porous carbon electrode and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid electrolyte will be discussed here. In addition, the derived depth-profile information (such as surface adsorption and multilayer formation) will be compared with the number density profiles of cation/anions calculated from the optimized MD simulations.

IS-TuP3 Bimetallic Nanoparticles Stability Investigated by In Situ XPS and TEM. *Cecile Bonifacio*, University of Pittsburgh, *S.C. Carenco*, *M.B. Salmeron*, Lawrence Berkeley National Laboratory, *J.C. Yang*, University of Pittsburgh

Bimetallic Ni and Co nanoparticles (NPs) possess intriguing potential for industrial applications due their remarkable catalytic activity for methane production and selective CO₂ reduction. Synthesizing these NPs as a core-shell structure presents a cost-effective way to produce catalysts by using the less expensive metal in the core and the more expensive but active metal catalyst in the shell. The core-shell structure can also allow for the fine tuning of reactivity, aversion of sintering issues for the core material, and even enhancement of tolerance to high temperatures. Unfortunately, NPs

tend to be unstable at temperatures far below their bulk melting temperature. In this work, the structural stability of Ni-Co core-shell was studied using *in situ* techniques. The morphological, structural, and chemical changes involved in the core-shell reconfiguration were examined during *in situ* annealing through simultaneous imaging and acquisition of elemental maps in the transmission electron microscope (TEM), and acquisition of O 1s, Ni 3p, and Co 3p x-ray photoelectron spectra (XPS). By observing the structural rearrangements of the nanoparticles *in situ* as a function of temperature, we were able to determine the thermal conditions under which the as-synthesized structure is stable and the minimum temperature where significant elemental diffusion and aggregation occurs. The NPs were annealed *in situ* in the TEM and XPS from 80°C to 650°C under vacuum conditions. Energy-dispersive x-ray spectroscopy (EDS) maps were acquired after each annealing step, yielding the quantitative distribution of Ni and Co within the NPs. Our results show that core-shell reconfiguration occurred in a stepwise process of surface oxide removal and metal segregation. Removal of the stabilizing surface oxide occurred from 320°C to 440°C, initiating the core-shell reconfiguration. Above 440°C, Ni migration from the core to the shell disrupted the core-shell structure of the NP leading to the subsequent formation of a homogeneous Ni-Co mixed alloy at 600°C. This work impacts other fields besides catalysis – including metallurgy, magnetism, etc. – where nanoparticle stability under operating conditions is essential for their technical viability and long-term durability.

Wednesday Morning, October 21, 2015

In-Situ Spectroscopy and Microscopy Focus Topic

Room: 211C - Session IS+AS+SA+SS-WeM

In-situ Studies Using X-ray Absorption Spectroscopy and Vibrational Spectroscopy for Catalytic and Energy Materials

Moderator: Franklin (Feng) Tao, University of Kansas, Zili Wu, Oak Ridge National Laboratory

8:00am **IS+AS+SA+SS-WeM1 In Situ X-ray Absorption Spectroscopy Technique for Metal/Water Interface Characterization, Chenghao Wu***, University of California, Berkeley and Lawrence Berkeley National Laboratory, *J.-H. Guo, M.B. Salmeron*, Lawrence Berkeley National Laboratory

Most of the electrochemistry processes occur within the thin layer of electrolyte at the electrolyte/electrode interfaces, commonly denoted as the electrical double layer (EDL). Although some classic continuum theories about EDL have been established and widely accepted over the past century, very little experimental information is available regarding the molecular-level details at such solid/liquid interfaces. We have developed in-situ liquid cells to study such solid/liquid interfaces by means of soft x-ray absorption spectroscopy [1]. Because the fluorescence x-ray photon has much larger mean free path in condensed matters than the secondary electrons, by comparing the total fluorescence yield (TFY) and total electron yield (TEY) spectra, we can extract useful information about the compositional, structural or chemical difference between the bulk and the interfacial electrolyte. Under different bias, by modulating the incident x-ray, the TEY signal current becomes alternating and can be separated from the dominant faradaic current so that we can obtain surface-sensitive TEY signal under electrochemical conditions.

With this *in-situ* and *operando* XAS technique, we investigated the gold/water interface [1] and platinum/sulfuric acid solution interface. It was found that at gold/water interface, the interfacial water layer has significantly different hydrogen-bonding network structure compared to the bulk water. Under different bias, the polar water molecules respond to the external electrical field and reorient at the gold electrode surface, which significantly changes the amount of distorted or broken hydrogen bonds. First-principle simulations were able to corroborate the experimental results and qualitatively reproduce the change in the x-ray absorption spectra at different bias. In the platinum/sulfuric acid system, the charged solute species, such as SO_4^{2-} ions, hydronium ions, introduce extra complexity at the surface under different bias. Using the same *in-situ* technique, we were also able to identify some intermediate surface species in the potential window of OER reaction.

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8:20am **IS+AS+SA+SS-WeM2 Tip Enhanced Raman Spectroscopy (TERS) of Graphene Nano-Ribbons and Graphene on Au Surfaces: Imaging and Vibrational Spectroscopy of Surface Reaction Products, Delroy Baugh, S. Liu, T. Kumagai, M. Wolf**, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

Tip Enhanced Raman Spectroscopy (TERS) is currently one of the most powerful probe techniques available and could be used to study reactions on surfaces at the single molecule level. TERS combines two very well developed techniques scanning probe microscopy (SPM), used to image single molecules on surfaces, and surface enhanced Raman spectroscopy (SERS), used to characterize vibrational spectra also of single molecules on surfaces. TERS could therefore provide unique and heretofore unprecedented insight on adsorbate reactions at the single-molecule level, e.g., image a molecule while it evolves from reactant to product at well defined surface sites as well as monitor vibrational spectra to provide bond specific information about the reaction. However, in order to clarify the vibrational structure in TERS, the details of the enhancement mechanism and the issues regarding the plasmonic background that is almost always observed in TER spectra as well the "blinking" that occurs in the SERS part of TERS must be resolved. Towards this end here we will report studies of Graphene and Graphene Nanoribbons (GNR's) on Au surfaces as a model systems because their electronic and vibrational structure are clearly defined. Specifically, Near and Far-field Raman spectra will be reported for

these systems and the above issues will be addressed experimentally and a simple theoretical model will be presented for the TERS observations.

8:40am **IS+AS+SA+SS-WeM3 Isomerization of One Molecule Observed through Tip-Enhanced Raman Spectroscopy: Azobenzene Thiol on Au(111), Joonhee Lee, N. Tallarida, L. Rios, V.A. Apkarian**, University of California, Irvine

The reversible *cis-trans* isomerization of a single azobenzene thiol (ABT) molecule is captured in tip-enhanced Raman trajectories in which the anti-correlated flip-flop between discrete, on and off-states of the two structural isomers is seen. The strongly blue-shifted spectra are recorded from a molecule that appears at the junction plasmon of a scanning tunneling microscope (STM), consisting of an atomically flat Au(111) surface and a silver tip. The variation in frequencies of switching events identifies heterogeneously photocatalyzed chemistry. The chemisorbed ensemble of ABT molecules lie flat on Au(111) surface with azobenzene headgroup strongly coupled to the surface. Nevertheless, we establish through STM imaging that the ABT molecules undergo both current driven and photoinduced *cis-trans* isomerization. Rather than decoupling from the surface, we suggest that strong coupling of the reaction coordinate to a vibrational energy sink is required for *cis-trans* isomerization of azobenzenes on metal surfaces.

9:00am **IS+AS+SA+SS-WeM4 In Situ Characterization and Reaction Studies of $\text{MnO}_x/\text{Co}_3\text{O}_4$ Catalyst for CO and CO_2 Conversion, Walter Ralston, G. Melaet**, University of California, Berkeley, *S. Alayoglu*, Lawrence Berkeley National Laboratory (LBNL), *G.A. Somorjai*, University of California, Berkeley

As the energy and fuel demands of our growing world continue to increase, non-fossil fuel carbon sources are increasingly attractive – especially if these carbon sources can be easily converted to transportable fuels and higher-value chemicals. Much attention has been focused on carbon dioxide, as capture and storage technology has emerged to mitigate emissions and CO_2 can be used to produce methanol.

Recently, we reported a catalyst for the low-pressure conversion of CO_2 to methanol¹. Manganese oxide nanoparticles supported in mesoporous Co_3O_4 produced methanol in high yields and at significantly lower pressure conditions than typical Cu/ZnO catalysts used industrially. The advantage of this catalyst is in its lower pressure requirement, its high yield of methanol, and its evidence of carbon-carbon bond formation (10% ethylene production).

Catalytic testing of the material has shown the catalyst to be more than the sum of its parts; when each component is tested separately (MnO_x nanoparticles supported in SiO_2 ; mesoporous Co_3O_4 alone) CH_4 and CO are the major products. Preparation and testing of an inverse catalyst – CoO_x nanoparticles on a mesoporous MnO_2 support – proves the importance of the hybrid architecture in determining the selectivity of the catalyst, as the inverse catalyst is dominated by the selectivity of the support (>80% selective to CO).

Towards understanding this catalyst, in-situ X-ray Absorption Spectroscopy (XAS) utilizing both soft and hard x-ray energies has allowed for a detailed characterization of the catalyst under oxidation, reduction, and reaction conditions. In addition to CO_2 , in-situ characterization under CO hydrogenation conditions was used to understand the Fischer-Tropsch activity of the catalyst for making longer chain hydrocarbons. The results of these in-situ studies are correlated with catalytic reaction data to help understand the nature of the active site/interface and guide future catalyst design.

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9:20am **IS+AS+SA+SS-WeM5 In Situ and Operando Raman Methodology to Understand the States of Oxide Catalysts and Alkane Oxidative Dehydrogenation and Ammoxidation Reactions, Miguel A. Bañares**, Instituto de Catálisis y Petroleoquímica, Madrid **INVITED**

Operando methodology combines in situ spectroscopy during reaction with simultaneous performance measurement in a cell that behaves like a catalytic reactor. Operando methodology connects changes in the performance and in the structure in a simultaneous manner; this is fundamental to assess the structure-performance relationships at a molecular level.

Molecularly dispersed vanadia on oxide carriers is a key component in many catalytic formulations in environmental and selective oxidation and

* ASSD Student Award Finalist

ammoxidation catalysis. The actual state of vanadia catalysts in specific environments depends on its surface density, the nature of the support and the presence of additives. We will summarize our experience on the state of supported vanadia paying particular attention to how the environment and reaction conditions finally shape the structure of vanadia catalysts. *Operando* Raman spectroscopy is an invaluable approach to fully understand the actual state of the catalyst, its transformations during reaction and how these correlate with changes in catalytic performance.

A single technique, may not deliver the complete vista, thus collaboration with complementary talents and techniques is critical. We show the outcome of collaborations with theoretical chemistry approaches to bring the rationale behind structure-activity relationships inferred through *operando* Raman methodology. We also show the interaction with engineering approaches.

11:00am **IS+AS+SA+SS-WeM10 *Operando* Studies of Dynamic Restructuring of Working Catalysts by Correlated Imaging and Spectroscopy Probes, Anatoly Frenkel, Yeshiva University INVITED**

Understanding mechanisms of reactivity is often hindered by complexity of nanoscale supported metal catalysts. In the size range of 1-5nm, they feature a variety of structural motifs, sizes, shapes, compositions, degrees of crystalline order as well as multiple temporal scales. Hence, new experimental methodologies are called for, ones that are capable to capture not only the details of kinetic, dynamic and catalytic properties of metal clusters, but also their statistical distributions over ensemble of such clusters in a particular working catalyst, i.e., in reaction conditions. I will present our recent results obtained at the National Synchrotron Light Source, Advanced Light Source and Center for Functional Nanomaterials, where we combined x-ray absorption spectroscopy, high resolution transmission electron microscopy and micro-IR spectroscopy studies of a complex catalytic system *in operando*, using the same portable micro-reactor. This method will be illustrated on the example of supported Pt and Pd catalysts undergoing dynamic restructuring during ethylene hydrogenation reaction. Our results demonstrate a complexity of structures exhibited in this system and their dynamic, responsive transformations throughout changing reaction conditions. The new method is both general and generalizable to quantitative *operando* studies of complex material systems of broad interest to areas as diverse as catalysis science, applied physics and materials science, using a wide variety of x-ray and electron based experimental probes.

11:40am **IS+AS+SA+SS-WeM12 A Correlation of Raman and Single and Multiple Layer Graphene Conductivity as Detected with a Cryogenic Multiprobe AFM with On-line Raman, NSOM and Other SPM Modalities, Aaron Lewis, The Hebrew University of Jerusalem and Nanonics Imaging Ltd, Israel, O. Zinoviev, A. Komissar, E. Maayan, D. Lewis, Nanonics Imaging Ltd, Jerusalem, Israel**

It is a challenge to study 2D materials, such as Graphene, MoS₂, WSe₂, etc. at temperatures down to 10°K when one considers the wide variety of physical phenomena that have to be applied to get a full picture of the functionality of these materials. This involves questions of structure, nanometric photoconductivity, electrical properties, thermal properties, near-field optical in the apertured and scattering modes, Kelvin probe, and of course Raman. All of these phenomena are common not only to 2D materials but also to carbon nanotubes and related nanomaterials. This presentation will describe both the instrumental development of such a multiprobe cryogenic system that allows for state of the art on-line optical measurements and will also include a review of the probe developments that permit such multifunctional multiprobe operation with on-line full optical access. The system that will be described has a completely free optical axis from above and below that is not obscured by electrical or other probes that have been developed for this system for multiprobe operation. This permits on-line Raman and Tip Enhanced NanoRaman Scattering. With such a system we have investigated graphene and HfO₂ using multiprobe electrical, Kelvin probe, NSOM and on-line Raman. The results have yielded new insights into the chemical changes that are correlated to the electrical conductivity.

12:00pm **IS+AS+SA+SS-WeM13 Surface Structure and Chemistry of Rh(110)-1×2 Under Reaction Condition and During Catalysis explored with AP-XPS and HP-STM, Franklin (Feng) Tao, L. Nguyen, University of Kansas**

High pressure scanning tunneling microscopy (HP-STM), ambient pressure X-ray photoelectron spectroscopy (AP-XPS), and computational studies were used to study the surface chemistry and structure of Rh(110)-1×2 and Rh(110)-1×1 at atomic scale in CO at different pressure and different temperature, and during CO oxidation at different pressure and different temperature. In gas of CO at a low pressure of 8×10^{-8} Torr, a Rh(110)-1×2 covered with CO is formed at 25C by replacing the adsorbed oxygen atoms

adsorbed on Rh(110)-1×2 by CO molecules of gas phase. A pressure dependent structure of adsorbate layer of CO on Rh(110)-1×2 was revealed. In gas of CO at a high pressure of 0.08 Torr, the portion of CO molecules bound in atop configuration in the adsorbed layer increases along with the increase of pressure of CO gas though there is no restructuring of Rh(110)-1×2 at 25C in the pressure range of 8×10^{-8} to 0.8 Torr. This is supported by the calculated coverage-dependent binding energy of CO on this surface. At a relatively high temperature of 55C, Rh(110)-1×2 in 0.08 Torr CO is restructured to Rh(110)-1×1 (Figure 1b). This temperature of surface restructuring is much lower than 153C for Rh(110)-1×2 in UHV. Theoretical simulation suggests that adsorbed CO molecules promote this restructuring compared to the restructuring in UHV since adsorption of CO on the intermediate structures of this restructuring in gas of CO lower the activation barrier of these intermediate structures. Rh(110)-1×2 is restructured to Rh(110)-1×1 during catalysis in the mixture of CO (0.08 Torr) and O₂ (0.02 Torr) even at 25C. Compared to the lack of restructuring in pure CO of 0.08 Torr at 25C, this restructuring during catalysis could result from a local heating of the catalyst surface by the exothermic reaction of CO oxidation. During CO oxidation, certain number of CO molecules are still remained on the catalyst surface. In the temperature range of 50-130C the active phase of catalysis is metallic Rh(110)-1×1. However, at 200C the active phase is surface rhodium oxide. These in-situ studies of surface structure and chemistry integrated with computational studies of Rh(110) in pure CO and in mixture of CO and O₂ clearly demonstrate the complexity of surface structure of a catalyst under reaction condition and during catalysis. The pressure-dependent structure of adsorbate layer, temperature-driven surface restructurings, generation of a new active surface phase of catalyst during catalysis, suggest the significance of in-situ studies of structure and chemistry of surface of a catalyst during catalysis.

Wednesday Afternoon, October 21, 2015

2D Materials Focus Topic

Room: 212C - Session 2D+EM+IS+MC+NS+SP+SS-WeA

Dopants and Defects in 2D Materials

Moderator: Daniel Gunlycke, Naval Research Laboratory, Zenghui Wang, Case Western Reserve University

2:20pm **2D+EM+IS+MC+NS+SP+SS-WeA1 The Effect of Defect Density on the Mechanical Properties of Graphene, Jonathan Willman, J.M. Gonzales, University of South Florida, R. Perriot, Los Alamos National Laboratory, I.I. Oleynik, University of South Florida**

Recent experiments involving nanoindentation of graphene have demonstrated counterintuitive weakening of Young's modulus with increasing concentrations of point defects in graphene in contradiction to previous investigations. To fully resolve these inconsistencies we perform large-scale molecular dynamics simulations of nanoindentation under conditions of Atomic Force Microscopy (AFM) nanoindentation experiments. The reliable description of interatomic interactions is achieved by using recently developed screened environment-dependent bond order (SED-REBO) potential. The elastic properties of the defective graphene, the breaking strength and the mechanisms of fracture under indenter are investigated as a function of type of point defects as well as their concentration.

2:40pm **2D+EM+IS+MC+NS+SP+SS-WeA2 Investigation of Grain Boundaries in CVD Grown MoS₂, Kolyo Marinov, D. Ovchinnikov, D. Dumcenco, A. Kis, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland**

We present the characterization of grain boundaries in polycrystalline CVD-grown MoS₂ films. Epitaxial growth on sapphire substrates is achieved leading to preferred orientation of the domains, which is confirmed by transmission electron microscopy experiments. Using Scanning Kelvin probe microscopy the local potential drop across the three predominant types of grain boundaries in field effect transistors is investigated. These measurements demonstrate that the interfaces between single grains do not degrade the electrical conductivity, which is due to the well aligned growth of the single domains. Furthermore, the relatively high mobility of electrons in the polycrystalline material stays constant even in devices with channels of 80 μm containing multiple grains, separated by grain boundaries. Our approach is a step forward to fabrication of large-area, uniform and high quality single-layer CVD MoS₂.

3:00pm **2D+EM+IS+MC+NS+SP+SS-WeA3 Polycrystalline 2D Materials: Atomic Structure and Electronic Transport Properties, Oleg Yazyev, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland**

INVITED

Grain boundaries and dislocations are intrinsic topological defects of polycrystalline materials, which inevitably affect their physical properties. In my talk, I will discuss the structure of topological defects in two-dimensional (2D) materials such as graphene and monolayer transition metal dichalcogenides (TMDCs) [1].

I will first introduce a general approach for constructing dislocations in graphene characterized by arbitrary Burgers vectors and grain boundaries covering the complete range of possible misorientation angles. By means of first-principles calculations we address the thermodynamic properties of grain boundaries revealing energetically favorable large-angle configurations as well as dramatic stabilization of small-angle configurations via the out-of-plane deformation, a remarkable feature of graphene as a two-dimensional material [2]. Both the presence of stable large-angle grain-boundary motifs and the out-of-plane deformation of small-angle configurations have recently been observed by scanning tunneling microscopy [3].

In the rest of my talk, I will focus on the electronic transport properties of polycrystalline 2D materials. Ballistic charge-carrier transmission across periodic grain boundaries is governed primarily by momentum conservation. Two distinct transport behaviors of such grain boundaries in graphene are predicted – either perfect reflection or high transparency with respect to low-energy charge carriers depending on the grain boundary periodicity [4]. It is also shown that certain periodic line defect structures can be engineered and offer opportunities for generating valley polarized charge carriers [5]. Beyond the momentum conservation picture we find that the transmission of low-energy charge carriers can be dramatically suppressed in the small-angle limit [6]. Unlike graphene, TMDCs combine a two-valley electronic band structure with strong spin-orbit effects. The

latter can be employed for creating spin-polarized currents and adds yet another conservation law in the electronic transport across regular defects such as the frequently observed inversion domain boundaries [7,8].

* This work has been supported by the Swiss NSF, ERC and Graphene Flagship.

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4:20pm **2D+EM+IS+MC+NS+SP+SS-WeA7 Defects Compensation and Refining Optical Luminescence in Organic/Transition Metal Dichalcogenide Heterostructure, J.H. Park, UC San Diego, A.M. Sanne, H.C.P. Movva, UT-Austin, S. Vishwanath, Cornell University, Il Jo Kwak, UC San Diego, H. Xing, Cornell University, J. Robertson, University of Cambridge, UK, S.K. Banerjee, UT-Austin, A.C. Kummel, UC San Diego**

Since layered transition-metal dichalcogenides (TMD) have demonstrated novel electronic and optoelectronic property, intense research has focused synthesis and integration into future electronic devices. Unlike graphene, TMD materials have band gaps, and these band structures can be tuned by thickness. However, in many cases, unintentional defects can be observed on TMD giving rise to the degradation of performance in the devices. Even for mechanical exfoliated TMD, there is a high density of defects, such as vacancies. For successful integration of TMD into devices, proper passivation of defects on TMD requires high stability in ambient conditions. In this study, a TiOPc monolayer was employed for passivation of defects to improve electrical and optical properties in TMD devices. Multilayer MoS₂ flakes were cleaved in ambient condition and transferred into the UHV chamber; afterwards, TiOPc monolayers were deposited on the MoS₂ surfaces by organic molecular beam epitaxy. After deposition, TiOPc forms a monolayer with only few defects, and the TiOPc monolayer structure has square lattice in a 1.5x1.5 nm grid. This crystal structure indicates that each TiOPc in the monolayer is directed outward to vacuum. The deposited TiOPc layer has very high thermal stability on MoS₂; the TiOPc layer on MoS₂ requires annealing above of 673K for desorption. This high thermal stability indicates there are strong interaction between TiOPc and MoS₂ surface. STS shows the band gap of the monolayer is 1.8 eV, while bulk MoS₂ has a 1.3eV band gap. Moreover, the Fermi level of TiOPc/bulk MoS₂ is shifted to the valence band, consistent with a P type shift. However, bulk MoS₂ surface, where less than monolayer of TiOPc was deposited, has Fermi level shifted towards the conduction band, consistent with N type doping. In the single layer MoS₂ deposited TiOPc monolayer, threshold bias is shifted from -30 V to near 0 V, indicating P-doping of MoS₂. It can be hypothesized that the work function transition of MoS₂ is changed as a function of thickness. Before deposition of the TiOPc monolayer, the defects peak corresponded to S vacancy is displayed at 1.7 eV in photoluminescence. Conversely, the deposition of TiOPc monolayer almost completely suppresses S vacancy peak located 1.7 eV. Moreover, in the single layer MoS₂ FET, the on/off ratio is enhanced more than 2 orders magnitude. The similar charge transfer behavior also can be observed in TiOPc/WSe₂; on the bilayer WSe₂/HOPG, the TiOPc monolayer deposited on the first layer of WSe₂ shows the a conduction band shifted Fermi level, while a TiOPc monolayer deposited on the second layer of WSe₂ shows a valence band shifted Fermi level.

4:40pm **2D+EM+IS+MC+NS+SP+SS-WeA8 Reactivity and Wettability of PVD Metals on 2D Transition Metal Dichalcogenides, Christopher Smyth, S. McDonnell, R. Addou, H. Zhu, C.L. Hinkle, R.M. Wallace, University of Texas at Dallas**

Transition metal dichalcogenides (TMDs) have been studied for years due to their tribological properties, but recent discoveries have illuminated unique opportunities for the use of single or few layer TMDs in electronics, specifically tunnel field effect transistors (TFETs). The properties of TFETs fabricated with single and few layer TMDs have been investigated with some degree of success, but it has been shown via in-situ chemical analysis that interface interactions between certain contact metals and the underlying TMD are not fully understood^{1,2}.

In this study, the wettability and reactivity of various metals with a number of bulk TMDs (MoS₂, HfSe₂, SnSe₂, etc.) were investigated. Multiple samples were processed in parallel to ensure that all sample sets saw

identical metal depositions. The metal-TMD interface was monitored in-situ using X-ray photoelectron spectroscopy (XPS) and metal film topography was imaged using atomic force microscopy (AFM). For some low work function metals, noticeable differences in interface chemistry were found between samples that saw high vacuum rather than UHV metal e-beam depositions.

Significant variations in compatibility between contact metal and TMD were discovered. These variations were dependent upon the metal-TMD pair and the base pressure of the chamber prior to metal deposition. Au exhibits far superior wettability on MoSe₂, where uniform thin films were achieved, compared to ReSe₂, on which Au grows as clusters. Au wettability varies between that of thin films and clusters for the other TMDs studied. An Au thin film deposited on SnSe₂ results in the formation of reaction products such as Sn metal, as evidenced by the evolution of different chemical states in the Sn 3d spectrum after deposition. Reactions between MoS₂ and Sc producing Mo metal occur when Sc is deposited in UHV instead of HV. These results provide further understanding for the critical interface between Sc and TMD in high performance TFETs.

This work was supported in part by NSF Award No. 1407765, the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA, and by the Southwest Academy on Nanoelectronics (SWAN) sponsored by the Nanoelectronic Research Initiative and NIST.

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5:00pm **2D+EM+IS+MC+NS+SP+SS-WeA9 Defects and Boundaries in 2D Materials: Correlating Electronic Properties to Atomic Structures, An-Ping Li**, Oak Ridge National Laboratory **INVITED**

The quest for novel two-dimensional (2D) materials has led to the discovery of hybrid heterostructures of graphene and other 2D atomic films, which provide us fascinating playground for exploring defects and boundaries in a variety of atomic layers. Even in graphene itself, there usually exist large amount of extended topological defects, such as grain boundaries and changes in layer thickness, which divide graphene into grains and domains. These interfaces and boundaries can break the lattice symmetry and are believed to have a major impact on the electronic properties, especially the transport, in 2D materials.

Here, we report on the electronic and transport properties of two types of defects studied by STM and multi-probe scanning tunneling potentiometry with a focus on the correlations to their atomic structures. The first type of defect is the monolayer-bilayer (ML-BL) boundaries in epitaxial graphene on SiC. By measuring the transport spectroscopy across individual ML-BL graphene boundaries, a greater voltage drop is observed when the current flows from monolayer to bilayer graphene than in the reverse direction, displaying an asymmetric electron transport upon bias polarity reversal [1, 2]. Interestingly, this asymmetry is not from a typical nonlinear conductance due to electron transmission through an asymmetric potential. Rather, it indicates the opening of an energy gap at the Fermi energy. Another type of defect is 1D interface in hexagonal boron nitride (hBN) and graphene planar heterostructures, where a polar-on-nonpolar 1D boundary is expected to possess peculiar electronic states associated with edge states of graphene and the polarity of hBN [2]. By implementing the concept of epitaxy to 2D space, we grow monolayer hBN from fresh edges of monolayer graphene with lattice coherence, forming a 1D boundary [3]. STM/STS measurements reveal an abrupt 1D zigzag oriented boundary, with boundary states about 0.6 eV below or above the Fermi level depending on the termination of the hBN at the boundary [4]. The boundary states are extended along the boundary, and exponentially decay into the bulk of graphene and hBN. The origin of boundary states and the effect of the polarity discontinuity at the interface will be discussed.

This research was conducted at the Center for Nanophase Materials Sciences, which is DOE Office of Science User Facility.

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5:40pm **2D+EM+IS+MC+NS+SP+SS-WeA11 Metal Ion Intercalated 2D Materials as Transparent Electrodes, Jiayu Wan***, W. Bao, F. Gu, University of Maryland, College Park, M. Fuhrer, Monash University, Malaysia, L. Hu, University of Maryland, College Park

Transparent electrode materials are critical for optoelectronic devices such as touch screen and solar cells. Graphene has been widely studied as transparent electrodes for its unique physical properties. To further boost the performance of graphene based transparent electrodes, we novelized Li-ion intercalation in graphene, and achieved highest performance of carbon based transparent electrodes. [1] Transmission as high as 91.7% with a sheet resistance of 3.0 ohm/sq is achieved for 19-layer LiC₆, which corresponds to a figure of merit (σ_{dc}/σ_{opt}) at 1,400, significantly higher than any other continuous transparent electrodes. The unconventional modification of ultrathin graphite optoelectronic properties is explained by the suppression of interband optical transitions and a small intraband Drude conductivity near the interband edge. To achieve low cost, large scale graphene-based transparent electrodes, we further developed Na-ion intercalated printed reduced graphene oxide (RGO) film [2]. Unlike pristine graphene that inhibits Na-ion intercalation, the larger layer-layer distance of RGO allows Na-ion intercalation, leading to simultaneously much higher DC conductivity and higher optical transmittance. The typical increase of transmittance from 36% to 79% and decrease of sheet resistance from 83 kohms/sq to 311 ohms/sq in the printed network was observed after Na-ion intercalation. Compared with Li-intercalated graphene, Na-ion intercalated RGO shows much better environmental stability, which is likely due to the self-terminating oxidation of Na ions on the RGO edges. This study demonstrated the great potential of metal-ion intercalation to improve the performance of graphene-based materials for transparent conductor applications.

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6:00pm **2D+EM+IS+MC+NS+SP+SS-WeA12 Oxygen Reduction Reaction on Nitrogen-doped Graphene, Jun Nakamura**, The University of Electro-Communications (UEC-Tokyo), Japan, A. Ichikawa, H. Matsuyama, A. Akaishi, The University of Electro-Communications (UEC-Tokyo)

Recently, several groups have reported high oxygen reduction reaction (ORR) activities in nitrogen-doped carbon nanomaterials which are candidates of metal-free catalysts for ORR [1]. Lee et al. have successfully fabricated nitrogen-doped graphene with the high ORR activity in acid media [2]. It has been confirmed that local atomic configurations of dopants in nitrogen-doped graphene are classified into three functional groups (pyrrole-like, pyridine-like, and graphite-like configurations) [3,4]. However, the mechanism of the ORR on the nitrogen-doped graphene has not fully understood.

In this work, we examine the ORR on the nitrogen-doped graphene containing the graphite-like N in a basal plane using first-principles calculations. In general, the ORR occurs mainly two pathways: The two-electron pathway (2e-) that is reduced to hydrogen peroxide (H₂O₂), and the direct four-electron pathway (4e-) that reduces to water (H₂O). Thermodynamic electrode potentials of each process at standard conditions are about 0.68V (2e-) and 1.23V (4e-), respectively. In case of the associative mechanism for the two- and four- electron reduction pathways, the electrocatalytic activity is governed by the stability of reaction intermediates like OOH*, OH*, and O* (where "*" refers to a surface site). Free energies of the reaction intermediates have been calculated based on the computational hydrogen electrode model suggested by Nørskov et al. [5]. We have taken account of effects of electrode potential, Ph of a solution, a local electric field in double layer, and water environment.

We have constructed energy diagrams at several electrode potentials on the basis of the first-principles calculations. It has been shown that the 2e- and 4e- reduction processes proceed at potentials up to about 0.5V and 0.8V, respectively. This means that we can control the reduction pathway for the nitrogen-doped graphene with the graphite-like N. Proton-electron transfer to OOH* (the 2e- pathway), and the formation of OOH* (the 4e- pathway) are confirmed to be the rate-limiting steps, respectively. Density dependence of N on the ORR activity will also be discussed in the presentation.

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In-Situ Spectroscopy and Microscopy Focus Topic
Room: 211B - Session IS+SS+NS+BI+VT+MN+AS-WeA

In situ Imaging of Liquids using Microfluidics
Moderator: Xiao-Ying Yu, Pacific Northwest National Laboratory, Stephen Nonnenmann, University of Massachusetts - Amherst

2:20pm **IS+SS+NS+BI+VT+MN+AS-WeA1 In Situ Multimodal Biological Imaging using Micro- and Nanofluidic Chambers, James Evans, C. Smallwood**, Pacific Northwest National Laboratory **INVITED**
 Biological organisms have evolved a number of spatially localized and highly orchestrated mechanisms for interacting with their environment. Since no single instrument is capable of probing the entire multidimensional landscape, it is not surprising that one of the grand challenges in biology remains the determination of how dynamics across these scales lead to observed phenotypes.

Therefore, there is a need for in-situ correlative multimodal and multiscale imaging to fully understand biological phenomena and how chemical or structural changes at the molecular level impact the whole organism. We have been advancing new methods for both cryogenic and in-situ correlative analysis of biological samples using electron, ion, optical and x-ray modalities. Central to this work is the development of new micro- and nanofluidic chambers that enable in-situ observations within precisely controlled liquid-flow environments. In this talk I will review the design of these new chambers, highlight current science applications and outline our future goals for adding additional functionality and expanding the versatility of the devices to other disciplines.

3:00pm **IS+SS+NS+BI+VT+MN+AS-WeA3 Glyoxal Aqueous Surface Chemistry by SALVI and Liquid ToF-SIMS, Xiao Sui, Y. Zhou, Z. Zhu**, Pacific Northwest National Laboratory, *J. Chen*, Shandong University, China, *X.-Y. Yu*, Pacific Northwest National Laboratory

Glyoxal, a ubiquitous water-soluble gas-phase oxidation product in the atmosphere, is an important source of oxalic acid, a precursor to aqueous secondary organic aerosol (SOA) formation. Many recent laboratory experiments and field observations suggest that more complex chemical reactions can occur in the aqueous aerosol surface; however, direct probing of aqueous surface changes is a challenging task using surface sensitive techniques. The ability to map the molecular distribution of reactants, reaction intermediates, and products at the aqueous surface are highly important to investigate surface chemistry driven by photochemical aging. In this study, photochemical reactions of glyoxal and hydrogen peroxide (H₂O₂) were studied by a microfluidic reactor, System for Analysis at the Liquid Vacuum Interface (SALVI), coupled with Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Aqueous surfaces containing glyoxal and hydrogen peroxide were exposed to UV light at variable lengths of time and were immediately analyzed in the SALVI microchannel by in situ liquid ToF-SIMS. In addition, various control samples were conducted to ensure that our findings were reliable. Compared with previous results of bulk solutions using ESI-MS, our unique liquid surface molecular imaging approach provided observations of glyoxal hydrolysis (i.e., first and secondary products, dimers, trimers, and other oligomers) and oxidation products (i.e., glyoxylic acid, oxalic acid and formic acid) with sub-micrometer spatial resolution. We potentially provide a new perspective and solution to study aqueous surface chemistry as an important source of aqueous SOA formation of relevance to atmospheric chemistry known to the community.

3:20pm **IS+SS+NS+BI+VT+MN+AS-WeA4 Investigating Shewanella Oneidensis Biofilm Matrix in a Microchannel by In Situ Liquid ToF-SIMS, Yuanzhao Ding**, Nanyang Technological University, Singapore, *X. Hua, Y. Zhou, J. Yu, X. Sui, J. Zhang, Z. Zhu*, Pacific Northwest National Laboratory, *B. Cao*, Nanyang Technological University, Singapore, *X.-Y. Yu*, Pacific Northwest National Laboratory

Biofilms consist of a group of micro-organisms attached onto surfaces or interfaces and embedded with a self-produced extracellular polymeric substance (EPS) in natural environments. The EPS matrix, like the "house of the cells", provides bacteria cells with a more stable environment and makes them physiologically different from planktonic cells. *Shewanella*

oneidensis MR-1 is a metal-reducing bacterium, forming biofilms that can reduce toxic heavy metals. This capability makes *S. oneidensis* biofilms very attractive in environmental applications. To better understand the biofilm EPS matrix composition at the interface, in situ chemical imaging with higher spatial resolution and more molecular level chemical information is strongly needed. Traditionally, electron microscopy and fluorescence microscopy are common imaging tools in biofilm research. However, the bottlenecks in these imaging technologies face the limitations that it is difficult for them to provide chemical information of small molecules (e.g., molecule weight <200). In this study, we use an emerging technology liquid Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) to observe *S. oneidensis* biofilm cultured in a vacuum compatible microchannel of the System for Analysis at the Liquid Vacuum Interface (SALVI) device. Chemical spatial distributions of small organic molecules that are considered to be the main building components of EPS in live biofilms are obtained. Principal component analysis is used to determine differences among biofilms sampled along the microchannel. This new approach overcomes previous limitations in live biofilm analysis and provides more chemical information of the EPS relevant to biofilm formation. Better understanding of the biofilm matrix will potentially fill in the knowledge gap in biofilm surface attachment and detachment processes and improve the engineering and design of *S. oneidensis* biofilms with high efficiencies in heavy metal reduction.

4:20pm **IS+SS+NS+BI+VT+MN+AS-WeA7 Ultrafast Proton and Electron Dynamics in Core-Level Ionized Aqueous Solution, Bernd Winter**, Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherung BESSY II, Germany **INVITED**

Photo- and Auger electron spectroscopy from liquid water reveals a novel electronic de-excitation process of core-level ionized water in which a pair of two cations forms, either H₂O⁺-H₂O⁺ or OH⁺-H₃O⁺. These reactive species are the delocalized analogue to H₂O²⁺, formed in a localized on-site Auger decay, and are expected to play a considerable role in water radiation chemistry. Both cationic pairs form upon autoionization of the initial ionized water molecule, and we are particularly interested in the situation where autoionization occurs from a structure that evolves from proton transfer, from the ionized water molecule to a neighbor molecule, within a few femtoseconds. The actual autoionization is either through intermolecular Coulombic decay (ICD) or Auger decay. Experimental identification of the proton dynamics is through isotope effects. A question that arises is whether such so-called proton-transfer mediated charge separation (PTM-CS) processes occur in other and similarly hydrogen-bonded solute molecules as well. This is indeed the case, and is illustrated here for ammonia and glycine in water, as well as for hydrogen peroxide in water, where characteristic differences are detected in the Auger-electron spectra from the light versus heavy species, i.e., NH₃ in H₂O versus ND₃ in D₂O, glycine(H) in H₂O versus glycine(D) in D₂O, and H₂O₂ in H₂O versus D₂O₂ in D₂O. The important spectral feature here is the high-kinetic energy tail of the Auger spectrum, which has no gas-phase analogue, and hence reflects the participation of solvent water in the relaxation process. The probability of the proton dynamics, judged from the intensities of the electron signal and inferred from methods of quantum chemistry and molecular dynamics, is found to depend on hydrogen-bond strength and hence on the specific hydration configuration. Favorable configurations for hydrogen peroxide(aq) occur due to the molecule's flexible structure. In ammonia(aq) the PTM processes are found to be less probable than for water(aq), which is attributed to the planarization of the ammonia molecule upon core-level ionization. The effect is smaller for the neutral -NH₂(aq) group of glycine at basic pH, where intramolecular dynamics is less likely. Nature and chemical reactivity of the initial transient species and their role for radiation chemistry and for local reactions relevant for biological molecules in an aqueous environment are discussed for the different molecular hydrogen-bonded systems.

5:00pm **IS+SS+NS+BI+VT+MN+AS-WeA9 Water Dissociation in Metal Organic Frameworks with Coordinatively Unsaturated Metal Ions: MOF-74, Kui Tan**, The University of Texas at Dallas, *S. Zuluaga*, Wake Forest University, *E. Fuentesf*, The University of Texas at Dallas, *H. Wang*, Rutgers University, *P. Canepa*, Wake Forest University, *J. Li*, Rutgers University, *T. Thonhauser*, Wake Forest University, *Y.J. Chabal*, The University of Texas at Dallas

Water dissociation represents one of the most important reactions in catalysis, essential to the surface and nano sciences. However, the dissociation mechanism on most oxide surfaces is not well understood due to the experimental challenges of preparing surface structures and characterizing reaction pathways. To remedy this problem, we propose the metal organic framework MOF-74 as an ideal model system to study water reactions. Its crystalline structure is well characterized; the metal oxide node mimics surfaces with exposed cations; and it degrades in water. Combining *in situ* IR spectroscopy and first-principles calculations, we

explored the MOF-74/water interaction as a function of vapor pressure and temperature. Here, we show that, while adsorption is reversible below the water condensation pressure (~19.7 Torr) at room temperature, a reaction takes place at ~150 °C even at low water vapor pressures. This important finding is unambiguously demonstrated by a clear spectroscopic signature for the direct reaction using D₂O, which is not present using H₂O due to strong phonon coupling. Specifically, a sharp absorption band appears at 970 cm⁻¹ when D₂O is introduced at above 150 °C, which we attribute to an O-D bending vibration on the phenolate linker. Although H₂O undergoes a similar dissociation reaction, the corresponding O-H mode is too strongly coupled to MOF vibrations to detect. In contrast, the O-D mode falls in the phonon gap of the MOF and remains localized. First-principles calculations not only positively identify the O-D mode at 970 cm⁻¹ but derive a pathway and kinetic barrier for the reaction and the final configuration: the D (H) atom is transferred to the oxygen of the linker phenolate group, producing the notable O-D absorption band at 970 cm⁻¹, while the OD (or OH) binds to the open metal sites. Experimental data and theoretical modeling further shows that the reaction is facilitated by a cooperative effect of several H₂O molecules. This finding explains water dissociation in this case and provides insight into the long-lasting question of MOF-74 degradation. Overall, it adds to the understanding of molecular water interaction with cation-exposed surfaces to enable development of more efficient catalysts for water dissociation.

Ref: K. Tan, S. Zuluaga, Q. Gong, P. Canepa, H. Wang, J. Li, Y. J. Chabal and T. Thonhauser, *Chem. Mater.*, 2014, **26**, 6886-6895.

5:20pm **IS+SS+NS+BI+VT+MN+AS-WeA10 Competitive Co-Adsorption of CO₂ with H₂O, NH₃, SO₂, NO, NO₂, N₂, O₂, and CH₄ in M-MOF-74 (M= Mg, Co, Ni): The Role of Hydrogen Bonding.** K. Tan, The University of Texas at Dallas, **Sebastian Zuluaga**, Wake Forest University, **H. Wang**, Rutgers University, **Y. Gao**, The University of Texas at Dallas, **J. Li**, Rutgers University, **T. Thonhauser**, Wake Forest University, **Y.J. Chabal**, The University of Texas at Dallas

The importance of co-adsorption for applications of porous materials in gas separation has motivated fundamental studies, which have initially focused on the comparison of the binding energies of different gas molecules in the pores (i.e. energetics) and their overall transport. By examining the competitive co-adsorption of several small molecules in M-MOF-74 (M= Mg, Co, Ni) with *in-situ* infrared spectroscopy and *ab initio* simulations, we find that the binding energy at the most favorable (metal) site is not a sufficient indicator for prediction of molecular adsorption and stability in MOFs. Instead, the occupation of the open metal sites is governed by kinetics, whereby the interaction of the guest molecules with the MOF organic linkers controls the reaction barrier for molecular exchange. Specifically, the displacement of CO₂ adsorbed at the metal center by other molecules such as H₂O, NH₃, SO₂, NO, NO₂, N₂, O₂, and CH₄ is mainly observed for H₂O and NH₃, even though SO₂, NO, and NO₂ have higher binding energies (~70-90 kJ/mol) to metal sites than that of CO₂ (38 to 48 kJ/mol) and slightly higher than water (~60-80 kJ/mol). DFT simulations evaluate the barriers for H₂O↔CO₂ and SO₂↔CO₂ exchange to be ~ 13 and 20 kJ/mol, respectively, explaining the slow exchange of CO₂ by SO₂, compared to water. Furthermore, the calculations reveal that the kinetic barrier for this exchange is determined by the specifics of the interaction of the second guest molecule (e.g., H₂O or SO₂) with the MOF ligands. Hydrogen bonding of H₂O molecules with the nearby oxygen of the organic linker is found to facilitate the positioning of the H₂O oxygen atom towards the metal center, thus reducing the exchange barrier. In contrast, SO₂ molecules interact with the distant benzene site, away from the metal center, hindering the exchange process. Similar considerations apply to the other molecules, accounting for much easier CO₂ exchange for NH₃ than for NO, NO₂, CH₄, O₂, and N₂ molecules. In this work, critical parameters such as kinetic barrier and exchange pathway are first unveiled and provide insight into the mechanism of competitive co-adsorption, underscoring the need of combined studies, using spectroscopic methods and *ab initio* simulations to uncover the atomistic interactions of small molecules in MOFs that directly influence co-adsorption.

Ref: K. Tan, S. Zuluaga, Q. Gong, Y. Gao, N. Nijem, J. Li, T. Thonhauser and Y. J. Chabal, *Chem. Mater.*, 2015, **27**, 2203-2217.

6:00pm **IS+SS+NS+BI+VT+MN+AS-WeA12 In Situ STM Observation of Pd(110) Under the Hydrogen Pressure Between 10⁻⁶ Pa and 10⁻³ Pa.** **Jun Yoshinobu**, **H. Kikuchi**, **T. Koitaya**, **K. Mukai**, **S. Yoshimoto**, University of Tokyo, Japan

Hydrogen adsorption and absorption on/in Pd and Pd alloys are vital processes for the hydrogen storage and hydrogen permeation materials. We investigated the Pd(110) surface under the hydrogen pressures between 10⁻⁶ Pa and 10⁻³ Pa at room temperature using in-situ atom-resolved scanning tunneling microscopy (STM). We observed missing-atom, missing-row and added-row structures and the number of atoms in these structures were quantitatively analyzed as a function of exposure time. Note that adatoms

were not detected probably because they were mobile in the present experimental conditions. At 10⁻⁶ Pa, the numbers of missing-row and added-row atoms increased up to ~20 L (langmuir) and after that they were gradually reaching the saturation (steady-state). On the other hand, the number of missing-atoms decreased gradually from the initial stage. With increasing the hydrogen pressures the number of missing-row atoms and added-row atoms increased, and the whole surface was covered with these reconstructed structures after large exposures (>1000 L). It has been known that not only hydrogen adsorption but also hydrogen absorption occur in such conditions. Thus, the missing-row and added-row reconstructed structures are inevitable for hydrogen absorption on Pd(110).

2D Materials Focus Topic

Room: 212C - Session 2D+EM+IS+NS+PS+SP+SS-FrM

Surface Chemistry of 2D Materials: Functionalization, Membranes, Sensors

Moderator: Peter Sutter, University of Nebraska - Lincoln, Judy Cha, Yale University

8:20am **2D+EM+IS+NS+PS+SP+SS-FrM1 Chemically Modifying Graphene for Surface Functionality**, Paul Sheehan, S. Tsoi, S.C. Hernández, S.G. Walton, T.L. Reinecke, K.E. Whitener, J.T. Robinson, Naval Research Laboratory, R. Stine, Nova Research

Graphene has many superlative properties that may be tailored for specific applications, or even enhanced, through chemical functionalization. Chemical functionalization dramatically changes almost every critical property of graphene, changing it from opaque to transparent, from diamagnetic to ferromagnetic, from electron rich or electron poor, from electrically conducting to insulating (and back again!). This extensive control suggests that chemically modified graphene may aid applications from flexible sensors to surface engineering. I will discuss how stacks of 2D materials can control the dominant surface forces—van der Waals,¹ acid-base interactions, electrostatic interactions, etc.—and so surpass conventional methods of preparing surfaces with, for example, self-assembled monolayers. I will also briefly address goals as diverse as biosensing² or sloughing off chemical warfare agents.³

¹ ACS Nano, **2014**, 8 (12), pp 12410–12417

² BioTechniques, Vol. 57, No. 1, July 2014, pp. 21–30

³ ACS Nano. 2013 Jun 25;7(6):4746–55.

8:40am **2D+EM+IS+NS+PS+SP+SS-FrM2 Structural Phase Stability Control of Monolayer MoTe₂ with Adsorbed Atoms and Molecules**, Yao Zhou, E.J. Reed, Stanford University

Of the Mo- and W- dichalcogenide monolayers, MoTe₂ is particularly interesting because it exhibits a small energy difference (approximately 31 meV per MoTe₂) between its semiconducting 2H phase and metallic 1T' crystal structures. This feature makes it particularly interesting for potential phase change applications.

We study the adsorption of some common atoms and molecules onto monolayer MoTe₂ and the potential for adsorption to induce a phase change between the semiconducting 2H and metallic 1T' crystal structures of the monolayer. Using density functional theory with spin orbit and van der Waals energy contributions, we determined the most energetically favorable adsorption positions and orientations on the two phases of monolayer MoTe₂. We then obtained the formation energies for these adsorption reactions and found that atomic adsorption generally favors 1T' metallic phases while molecular adsorption favors semiconducting 2H phases. A possible application of this work may be the chemical stabilization of a preferred phase during the growth process.

Further, we consider the Mo_xW_{1-x}Te₂ alloy monolayers that exhibit even smaller energy difference between phases. Our calculations indicate that it may be possible to engineer an alloy (0 < x < 0.5) such that specific molecules will induce a phase change to 1T' while other molecules studied stabilize the 2H phase, which suggests that alloying may provide some molecular selectivity. This potentially provides the basis for molecular sensing applications due to the large electronic contrast between 2H and 1T' phases.

9:00am **2D+EM+IS+NS+PS+SP+SS-FrM3 Selective Nanochemistry on Graphene/Silicon Carbide: Substrate Functionalization and Polycyclic Aromatic Hydrocarbons Formation**, Patrick Soukiassian, CEA, France
INVITED

Graphene & silicon carbide (SiC) are advanced semiconductors having figures of merit scaling well above those of well-established ones [1,2]. Understanding/mediating SiC and graphene surfaces & interfaces properties are of central importance toward functionalization and applications. As a 2D material, graphene is a single atomic layer of carbon atoms in a sp² bonding configuration. Therefore, functionalization remains challenging since interacting too strongly with the graphene atomic layer may change its bonding configuration and properties. Instead, interacting with the SiC substrate offers an alternative approach. The 1st case of hydrogen-induced metallization of a semiconductor surface has been shown for a 3C-SiC(001) surface [3]. Here, combining investigations using advanced experimental techniques such as STM/STS, vibrational & 3rd generation synchrotron radiation-based photoelectron spectroscopies together with state-of-art

calculations will be presented and discussed. It includes: i) the 1st evidence of H/D-induced nanotunnel opening at a semiconductor sub-surface shown here for SiC [4]. Depending on H coverage, these nanotunnels could either be metallic or semiconducting. Dangling bonds generated inside the nanotunnels offer a promising template to capture atoms or molecules. These features open nano-tailoring capabilities towards advanced applications in electronics, chemistry, storage, sensors or biotechnology. Understanding & controlling such a mechanism open routes towards selective surface/interface functionalization of epitaxial graphene [4]. ii) The role of H interaction with graphene on SiC dust grains in polycyclic aromatic hydrocarbons (PAH) formation in the interstellar space with a possible route toward prebiotic roots of life in the universe [5].

1–W. Lu, P. Soukiassian, J. Boeckl “Graphene: fundamentals and functionalities” *MRS Bull.* **37**, 1119 (2012)

2–P. Soukiassian “Will graphene be the material of the 21th century?” *MRS Bull.* **37**, 1321 (2012)

3–V. Derycke, P. Soukiassian, F. Amy, Y.J. Chabal, M. D’angelo, H. Enriquez, M. Silly, “Nanochemistry at the atomic scale revealed in hydrogen-induced semiconductor surface metallization”, *Nature Mat.* **2**, 253 (2003)

4–P. Soukiassian, E. Wimmer, E. Celasco, Cl. Giallombardo, S. Bonanni, L. Vattuone, L. Savio, A. Tejada, M. Silly, M. D’angelo, F. Sirotti, M. Rocca “Hydrogen-induced nanotunnel opening within semiconductor subsurface” *Nature Com.* **4**, 2800 (2013)

5–P. Merino, M. Švec, J.I. Martinez, P. Jelinek, P. Lacovig, M. Dalmiglio, S. Lizzit, P. Soukiassian, J. Cernicharo, J.A. Martin-Gago “Graphene etching on SiC grains as a path to interstellar PAHs’ formation” *Nature Com.* **5**, 3054 (2014)

9:40am **2D+EM+IS+NS+PS+SP+SS-FrM5 Intrinsic Wettability of Graphene**, Haitao Liu, Department of Chemistry, University of Pittsburgh

Graphene and graphite are long believed to be hydrophobic. Here we show that a clean graphitic surface is in fact mildly hydrophilic [1]. We find that an as-prepared graphene sample is hydrophilic with a water contact angle of ca. 40°. Upon exposure to ambient air, the water contact angle gradually increased to ca. 60° within 20 min and plateaued at ca. 80° after 1 day. Infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) showed that airborne hydrocarbon adsorbed onto the graphene surface during this process. Both thermal annealing and controlled UV/O₃ treatment removed the hydrocarbon contaminants, which was accompanied by a concurrent decrease in the water contact angle. Our findings show that graphene is more hydrophilic than previously believed and suggest that the reported hydrophobic nature of graphene is due to unintentional hydrocarbon contamination from ambient air.

Reference

[1] Zhiting Li; et al.; Nature Materials, 12, 925-931, (2013)

10:00am **2D+EM+IS+NS+PS+SP+SS-FrM6 Au-doped Graphene As a Promising Electrocatalyst for the Oxygen Reduction Reaction in Hydrogen Fuel Cells: Prediction from First Principles**, Sergey Stolbov, University of Central Florida, M. Alcantara Ortigoza, Tuskegee University

One of the main obstacles hindering large scale practical application of hydrogen fuel cells is a prohibited cost of the Pt (or Pt-based) catalysts for the oxygen reduction reaction (ORR) on the fuel cell cathode. In this work, we consider Au-doped graphene as an alternative to Pt for facilitating ORR. Our first-principles calculations show that Au atoms incorporated into graphene di-vacancies form a thermodynamically and electrochemically stable structure. Furthermore, calculation of the binding energies of the ORR intermediates reveals that Au-C bonding makes the C atoms neighboring to Au optimally reactive for ORR. The calculated ORR free energy diagrams suggest that the Au-graphene structures have an ORR onset potential as high as that of Pt. We also demonstrate that the linear relation among the binding energy of the reaction intermediates assumed in a number of works on computational high-throughput material screening does not hold, at least for this none purely transition-metal material.

10:20am **2D+EM+IS+NS+PS+SP+SS-FrM7 Spontaneous Deposition of Palladium Nanoparticles on Graphene through Redox Reaction**, Xiaorui Zhang, W. Ooki, Y.R. Kosaka, T. Kondo, J. Nakamura, University of Tsukuba, Japan

Due to its unique properties such as huge surface area and excellent conductivity, graphene becomes great interesting for supporting noble metal catalysts. Some noble metals such as palladium, platinum, gold nanoparticles was reported to be able to spontaneous deposition on as-synthesized reduced graphene oxide with external reducing agent-free

recently. Yet the mechanism of spontaneous deposition of metals on graphene has not been clarified until now. In the present research, we spontaneously deposited palladium nanoparticles on as-synthesized reduced graphene oxide in H₂O medium without external reducing agent. It was found that the deposited amount of palladium varied with pH, meanwhile, the bivalent Pd²⁺ precursor was reduced to metallic palladium, and graphene was oxidized simultaneously with an increasing of its oxygen functional groups. The atomic ratio of the deposited Pd and the increased O in rGO located in a range from 1 to 2. As reducing agent-free, the mechanism on spontaneous redox deposition of metal nanoparticles on graphene was proposed, firstly, an efficient adsorption of metal precursor on graphene is a prerequisite which is determined by their electrical charges and adjusted by pH. Secondly, a positive galvanic potential between metal precursor and graphene is necessary for metal spontaneous deposition.

10:40am **2D+EM+IS+NS+PS+SP+SS-FrM8 Gradient Electrochemical Response of Template Synthesized Thickness Sorted MoS₂ Nanosheets for Cellular Level Free Radical Detection**, *Ankur Gupta, T. Selvan, S. Das, S. Seal*, University of Central Florida

The human body is a complex system capable of defending in adverse conditions. A classic example of such complex process is balanced equilibrium production between pro-oxidant and antioxidant in cells. However, when this equilibrium is disturbed, production of free radicals such as superoxide and nitric oxide strengthen, and causes serious cellular damages. Furthermore, myeloperoxidase (MPO) is released during the oxidative burst. This MPO combines with hydrogen peroxide (H₂O₂) and Cl⁻ and generate hypochlorous acid (HOCl). This is a short-lived and powerful diffusible oxidant strong oxidizer and could react with O²⁻ to produce OH⁻. Therefore, in physiological condition HOCl has a major role as a potent microbicidal agent in the immune defense; however, during the oxidative burst HOCl not only damage healthy tissue and generate radicals that are extremely reactive. Therefore, monitoring of the production of free radicals at the cellular level is important for diagnostic purpose. Over past years, several material have been used to develop sensors for free radical detection such as cerium oxide nanoparticles, MoS₂ nanosheets and nanoparticles. However, detection of free radicals at cellular level is still a challenge.

In this attempt, layered molybdenum disulfide (MoS₂) were synthesized via hydrothermal method. SBA-15 polymer template were utilized during hydrothermal process to grow MoS₂ around it to develop porosity. After the hydrothermal synthesis and washing, polymer template was removed by dissolving it in isopropanol which leaves high surface area layered MoS₂ crystal. Wet chemical exfoliation of MoS₂ were carried out in aqueous solution of Pluronic[®] F-127 having hydrophobic and hydrophilic chains. Pluronic[®] F-127 was used to bring down the buoyant density of MoS₂. Non-templated nanosheets were synthesized as control. The exfoliated solution were centrifuged at 3000 rpm to remove large particle and supernatant was collected for density gradient ultracentrifugation (DGU). Separation of different thickness layers is carried out by DGU. Thickness sort MoS₂ nanosheets were characterized using AFM, XPS, HRTEM, Raman and UV-Vis spectroscopy for structural and chemical analysis. XPS, HETEM and EFTEM analysis of nanosheets have illustrate the sulfur deficiency at the edges of the nanosheets. MoS₂ nanosheets were deposited on glassy carbon electrode for cyclic-voltammetry and chronoamperometry measurements. Higher sensitivity and repeatability were demonstrated by nanosheets prepared via template method as compared to control for reactive oxygen and nitrogen species, and HOCl.

11:00am **2D+EM+IS+NS+PS+SP+SS-FrM9 Methanol Synthesis on Defect-Laden Single-Layer MoS₂ Supported on Cu(111): Results of a First Principles Study**, *D. Le, Takat B. Rawal, T.S. Rahman*, University of Central Florida

Despite being found to be the preferred structure in single layer MoS₂, the sulfur vacancy row does not facilitate alcohol synthesis from syngas [1] because its narrow size limits adsorption, diffusion, and formation of possible intermediates. On the Cu(111) surface, strong interactions between MoS₂ and Cu are expected to reduce the corrugations caused by sulfur vacancy rows, resulting in a larger exposure of vacancies to adsorbates which could enhance the catalytic activity of the row towards alcohol synthesis from syngas. Based on the results of our density functional theory (DFT) simulations utilizing the DFT-D3 correction for accounting the van der Waals interactions, we show that: (1) there is a significant charge transfer from the Cu(111) surface to MoS₂, enhancing its catalytic properties, (2) the binding energies of CO and dissociated H₂ increase by 0.3 eV in comparison to that on unsupported MoS₂, indicating stronger interactions, and (3) the barriers for forming intermediate species in alcohol synthesis process reduce significantly in comparison to that on unsupported MoS₂. On the basis of these energetics, we conclude the Cu(111) substrate promotes methanol synthesis from syn gas on single-layer MoS₂ with a vacancy row. We will also present the energetic pathways for the

formations of other reaction products such as methane, formaldehyde, and water, as well as that of (the reverse) water gas-shift reaction.

[1] D. Le, T. B. Rawal, and T. S. Rahman, *J. Phys. Chem. C* **118**, 5346 (2014).

*This work is supported in part by the U.S. Department of Energy under grant DE-FG02-07ER15842

11:20am **2D+EM+IS+NS+PS+SP+SS-FrM10 The Happy Marriage of Graphene and Germanium: Graphene Achieves Exceptional Conductivity and Protects Germanium from Oxidizing**, *Richard Rojas Delgado*, University of Wisconsin-Madison, *F. Cavallo*, University of New Mexico, *R.M. Jacobberger, J.R. Sanchez Perez, D. Schroeder, M.A. Eriksson, M.S. Arnold, M.G. Lagally*, University of Wisconsin-Madison

The properties of graphene (G) make it an outstanding candidate for electronic-device applications, especially those that require no band gap but a high conductance. The conductance, involving both carrier mobility and carrier concentration, will depend critically on the substrate to which G is transferred. We demonstrate an exceptionally high conductance for G transferred to Ge(001) and provide an understanding of the mechanism.[1] Essential in this understanding is an interfacial chemistry consisting of Ge oxide and suboxide layers that provide the necessary charges to dope the graphene sheet, and whose chemical behavior is such that one can obtain long-term stability in the conductance. In contrast, when high-quality G is grown directly on Ge (100), (111), or (110), the conductance is unexceptional, but oxidation of the surface is significantly delayed and slowed, relative to both clean Ge and Ge with G transferred to its surface. [2,3] We fabricate Hall bars in G transferred to Ge and G grown using atmospheric-pressure CVD with methane precursors. X-ray photoelectron spectroscopy (XPS) is used to investigate the oxide in all stages of the measurements. The sheet resistance and Hall effect are measured from 300K to 10K for transferred and grown samples. Values of mobility and carrier concentration are extracted. It appears we have reached the highest combination of mobility and carrier concentration in graphene (suspended or supported) for temperatures from 10 to 300K. The implication is that the primary mechanisms for scattering charge in the G, roughness and a non-uniform electrostatic potential due to fixed charges, have limited effect when the substrate is oxidized Ge. Finally the subsequent oxidation kinetics of Ge (001) are compared for graphene directly grown on Ge and for graphene transferred to Ge. XPS shows that for graphene grown on Ge(001) the interface is oxide-free and remains so over long periods of time. For graphene transferred to Ge(001) the interface contains stoichiometric and substoichiometric oxides. The thickness of these oxides increases with time, but quite slowly. Using spatially resolved XPS, we propose a model of diffusion limited oxidation initiated at edges of the graphene.

Research supported by DOE.

[1]Cavallo, Francesca, et al. "Exceptional Charge Transport Properties of Graphene on Germanium." *ACS nano* 8.10 (2014): 10237-10245.

[2] R. M. Jacobberger, et al. "Oriented Bottom-Up Growth of Armchair Graphene Nanoribbons on Germanium." *Nature Comm.*, under review.

[3] R. Rojas, et. al "Passivation of Ge by Graphene.", in process.

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Amati, M.: IS+AS+SA+SS-MoA7, **4**
Andersen, J.N.: IS+AS+SS-MoM11, **2**
Apkarian, V.A.: IS+AS+SA+SS-WeM3, **11**
Armocost, M.D.: IS+AS+SA+SS-MoA10, **5**
Arnold, M.S.: 2D+EM+IS+NS+PS+SP+SS-FrM10, **18**

— B —

Bañares, M.A.: IS+AS+SA+SS-WeM5, **11**
Banerjee, S.K.:
2D+EM+IS+MC+NS+SP+SS-WeA7, **13**
Bao, W.: 2D+EM+IS+MC+NS+SP+SS-WeA11, **14**
Baugh, D.: IS+AS+SA+SS-WeM2, **11**
Belianinov, A.: IS+AS+SS-TuA11, **9**
Bluhm, H.: IS+AS+SS-MoM5, **2**
Bonifacio, C.S.: IS+AS+SS-TuA8, **8**; IS-TuP3, **10**
Broderick, A.: IS+AS+SA+SS-TuM2, **6**

— C —

Canepa, P.: IS+SS+NS+BI+VT+MN+AS-WeA9, **15**
Cao, B.: IS+SS+NS+BI+VT+MN+AS-WeA4, **15**
Carencio, S.C.: IS+AS+SS-TuA8, **8**; IS-TuP3, **10**
Cavallo, F.: 2D+EM+IS+NS+PS+SP+SS-FrM10, **18**
Chabal, Y.J.: IS+SS+NS+BI+VT+MN+AS-WeA10, **16**;
IS+SS+NS+BI+VT+MN+AS-WeA9, **15**
Chaudhary, S.: IS+AS+SS-MoM11, **2**
Chen, J.: IS+SS+NS+BI+VT+MN+AS-WeA3, **15**
Chen, P.: IS+AS+SA+SS-TuM10, **6**
Chen, X.: IS+AS+SS-MoM3, **1**
Craver, B.: IS+AS+SA+SS-MoA10, **5**
Crozier, P.A.: IS+AS+SS-TuA1, **8**
Crumlin, E.J.: IS+AS+SA+SS-TuM12, **6**;
IS+AS+SA+SS-TuM3, **6**; IS-TuP1, **10**

— D —

Das, S.: 2D+EM+IS+NS+PS+SP+SS-FrM8, **18**
De Lucia, F.C.: IS+AS+SA+SS-MoA10, **5**
Delgass, W.N.: IS+AS+SS-MoM8, **2**
Ding, Y.: IS+SS+NS+BI+VT+MN+AS-WeA4, **15**
Dumcenco, D.:
2D+EM+IS+MC+NS+SP+SS-WeA2, **13**
Dupuis, V.: IS+AS+SS-MoM3, **1**

— E —

Eichhorn, B.: IS+AS+SS-MoM5, **2**
Eren, B.: IS+AS+SA+SS-MoA5, **4**
Eriksson, M.A.:
2D+EM+IS+NS+PS+SP+SS-FrM10, **18**
Evans, J.E.: IS+SS+NS+BI+VT+MN+AS-WeA1, **15**
Ewing, P.R.: IS+AS+SA+SS-MoA10, **5**

— F —

Favaro, M.: IS+AS+SA+SS-TuM12, **6**;
IS+AS+SA+SS-TuM3, **6**
Foster, M.: IS+AS+SS-MoM6, **2**

Frenkel, A.: IS+AS+SA+SS-MoA3, **4**;
IS+AS+SA+SS-MoA8, **5**;
IS+AS+SA+SS-WeM10, **12**
Frenken, J.W.M.: IS+AS+SS-MoM4, **1**
Fuentef, E.: IS+SS+NS+BI+VT+MN+AS-WeA9, **15**
Fuhrer, M.: 2D+EM+IS+MC+NS+SP+SS-WeA11, **14**

— G —

Gao, Y.: IS+SS+NS+BI+VT+MN+AS-WeA10, **16**
Gonzales, J.M.:
2D+EM+IS+MC+NS+SP+SS-WeA1, **13**
Gounder, R.: IS+AS+SS-MoM8, **2**
Greeley, J.: IS+AS+SS-MoM8, **2**
Gregoratti, L.: IS+AS+SA+SS-MoA7, **4**
Groot, I.M.N.: IS+AS+SS-MoM4, **1**
Gu, F.: 2D+EM+IS+MC+NS+SP+SS-WeA11, **14**
Guo, J.-H.: IS+AS+SA+SS-WeM1, **11**
Gupta, A.: 2D+EM+IS+NS+PS+SP+SS-FrM8, **18**

— H —

Hartl, M.: IS+AS+SS-MoM5, **2**
Head, A.R.: IS+AS+SS-MoM11, **2**;
IS+AS+SS-MoM5, **2**
Helal, Y.H.: IS+AS+SA+SS-MoA10, **5**
Heldebrant, D.: IS+AS+SA+SS-TuM13, **7**
Hemminger, J.C.: IS+AS+SA+SS-TuM5, **6**
Hernández, S.C.:
2D+EM+IS+NS+PS+SP+SS-FrM1, **17**
Hinkle, C.L.: 2D+EM+IS+MC+NS+SP+SS-WeA8, **13**
Hu, L.: 2D+EM+IS+MC+NS+SP+SS-WeA11, **14**
Hua, X.: IS+SS+NS+BI+VT+MN+AS-WeA4, **15**
Hussain, Z.: IS+AS+SA+SS-TuM12, **6**;
IS+AS+SA+SS-TuM3, **6**

— I —

Iberi, V.: IS+AS+SS-TuA11, **9**
Ichikawa, A.: 2D+EM+IS+MC+NS+SP+SS-WeA12, **14**

— J —

Jacobberger, R.M.:
2D+EM+IS+NS+PS+SP+SS-FrM10, **18**
Jeon, B.: IS+AS+SA+SS-TuM3, **6**
Jeong, B.: IS+AS+SA+SS-TuM12, **6**
Johansson, N.: IS+AS+SA+SS-MoA4, **4**;
IS+AS+SS-MoM11, **2**
Joy, D.C.: IS+AS+SS-TuA11, **9**

— K —

Karslioglu, O.: IS+AS+SS-MoM5, **2**
Kaspar, T.C.: IS-TuP2, **10**
Khadra, G.: IS+AS+SS-MoM3, **1**
Khalifa, Y.: IS+AS+SA+SS-TuM2, **6**
Kikuchi, H.: IS+SS+NS+BI+VT+MN+AS-WeA12, **16**
Kipreos, M.: IS+AS+SS-MoM6, **2**
Kis, A.: 2D+EM+IS+MC+NS+SP+SS-WeA2, **13**
Knudsen, J.: IS+AS+SS-MoM11, **2**
Koitaya, T.: IS+SS+NS+BI+VT+MN+AS-WeA12, **16**
Kolmakov, A.: IS+AS+SA+SS-TuM4, **6**
Komissar, A.: IS+AS+SA+SS-WeM12, **12**
Kondo, T.: 2D+EM+IS+NS+PS+SP+SS-FrM7, **17**
Kosaka, Y.R.: 2D+EM+IS+NS+PS+SP+SS-FrM7, **17**
Kumagai, T.: IS+AS+SA+SS-WeM2, **11**
Kummel, A.C.:
2D+EM+IS+MC+NS+SP+SS-WeA7, **13**

Kuwauchi, Y.: IS+AS+SS-TuA3, **8**
Kwak, I.J.: 2D+EM+IS+MC+NS+SP+SS-WeA7, **13**

— L —

Lagally, M.G.: 2D+EM+IS+NS+PS+SP+SS-FrM10, **18**
Lao, D.: IS+AS+SA+SS-TuM13, **7**
Le, D.: 2D+EM+IS+NS+PS+SP+SS-FrM9, **18**
Lee, J.: IS+AS+SA+SS-TuM12, **6**;
IS+AS+SA+SS-WeM3, **11**
Lewis, A.: IS+AS+SA+SS-WeM12, **12**
Lewis, D.: IS+AS+SA+SS-WeM12, **12**
Li, A.-P.: 2D+EM+IS+MC+NS+SP+SS-WeA9, **14**
Li, J.: IS+AS+SA+SS-MoA3, **4**;
IS+SS+NS+BI+VT+MN+AS-WeA10, **16**;
IS+SS+NS+BI+VT+MN+AS-WeA9, **15**
Liu, H.: 2D+EM+IS+NS+PS+SP+SS-FrM5, **17**
Liu, J.: IS+AS+SA+SS-MoA8, **5**
Liu, Q.: IS+AS+SS-TuA1, **8**; IS-TuP1, **10**
Liu, S.: IS+AS+SA+SS-WeM2, **11**
Liu, Z.: IS+AS+SA+SS-TuM12, **6**;
IS+AS+SA+SS-TuM3, **6**; IS-TuP1, **10**

— M —

Maayan, E.: IS+AS+SA+SS-WeM12, **12**
Mao, B.H.: IS-TuP1, **10**
Marinov, K.M.:
2D+EM+IS+MC+NS+SP+SS-WeA2, **13**
Matsuyama, H.:
2D+EM+IS+MC+NS+SP+SS-WeA12, **14**
McClimon, J.B.: IS+AS+SA+SS-MoA4, **4**
McDonnell, S.:
2D+EM+IS+MC+NS+SP+SS-WeA8, **13**
Melaet, G.: IS+AS+SA+SS-WeM4, **11**
Miller, B.K.: IS+AS+SS-TuA1, **8**
Miller, J.: IS+AS+SS-MoM8, **2**
Monazami, E.: IS+AS+SA+SS-MoA4, **4**
Movva, H.C.P.:
2D+EM+IS+MC+NS+SP+SS-WeA7, **13**
Mukai, K.: IS+SS+NS+BI+VT+MN+AS-WeA12, **16**
Mun, B.S.: IS+AS+SA+SS-TuM12, **6**

— N —

Nakamura, J.: 2D+EM+IS+MC+NS+SP+SS-WeA12, **14**;
2D+EM+IS+NS+PS+SP+SS-FrM7, **17**
Nandasiri, M.L.: IS-TuP2, **10**
Neese, C.F.: IS+AS+SA+SS-MoA10, **5**
Newberg, J.: IS+AS+SA+SS-TuM2, **6**
Nguyen, L.: IS+AS+SA+SS-MoA3, **4**;
IS+AS+SA+SS-MoA8, **5**;
IS+AS+SA+SS-WeM13, **12**
Nune, S.: IS+AS+SA+SS-TuM13, **7**

— O —

Oleynik, I.I.: 2D+EM+IS+MC+NS+SP+SS-WeA1, **13**
Omote, H.: IS+AS+SS-TuA3, **8**
Ooki, W.: 2D+EM+IS+NS+PS+SP+SS-FrM7, **17**
Ovchinnikov, D.:
2D+EM+IS+MC+NS+SP+SS-WeA2, **13**
Ovchinnikova, O.S.: IS+AS+SS-TuA11, **9**

— P —

Park, J.H.: 2D+EM+IS+MC+NS+SP+SS-WeA7, **13**
Perriot, R.: 2D+EM+IS+MC+NS+SP+SS-WeA1, **13**
Phillip, N.D.: IS+AS+SS-TuA11, **9**

— R —

Rahman, T.S.: 2D+EM+IS+NS+PS+SP+SS-FrM9, 18
Ralston, W.: IS+AS+SA+SS-WeM4, 11
Rawal, T.B.: 2D+EM+IS+NS+PS+SP+SS-FrM9, 18
Reed, E.J.: 2D+EM+IS+NS+PS+SP+SS-FrM2, 17
Reinecke, T.L.:
2D+EM+IS+NS+PS+SP+SS-FrM1, 17
Reinke, P.: IS+AS+SA+SS-MoA4, 4
Ribeiro, F.: IS+AS+SS-MoM8, 2
Rios, L.: IS+AS+SA+SS-WeM3, 11
Robertson, J.: 2D+EM+IS+MC+NS+SP+SS-WeA7, 13
Robinson, J.T.:
2D+EM+IS+NS+PS+SP+SS-FrM1, 17
Rojas Delgado, R.:
2D+EM+IS+NS+PS+SP+SS-FrM10, 18
Rondinone, A.J.: IS+AS+SS-TuA11, 9
Ross, P.N.: IS+AS+SA+SS-TuM12, 6;
IS+AS+SA+SS-TuM3, 6

— S —

Salmeron, M.B.: IS+AS+SA+SS-MoA5, 4;
IS+AS+SA+SS-WeM1, 11; IS+AS+SS-TuA8, 8; IS-TuP3, 10
Sanchez Perez, J.R.:
2D+EM+IS+NS+PS+SP+SS-FrM10, 18
Sanne, A.M.: 2D+EM+IS+MC+NS+SP+SS-WeA7, 13
Schlögl, R.: IS+AS+SA+SS-MoA1, 4
Schnadt, J.: IS+AS+SA+SS-MoA4, 4;
IS+AS+SS-MoM11, 2
Schneider, W.F.: IS+AS+SS-MoM8, 2
Schroeder, D.: 2D+EM+IS+NS+PS+SP+SS-FrM10, 18
Schwarz, A.: IS-TuP2, 10
Seal, S.: 2D+EM+IS+NS+PS+SP+SS-FrM8, 18
Seifert, S.: IS+AS+SS-MoM3, 1
Selvan, T.: 2D+EM+IS+NS+PS+SP+SS-FrM8, 18
Sezen, H.: IS+AS+SA+SS-MoA7, 4
Shayesteh, P.: IS+AS+SA+SS-MoA4, 4
Sheehan, P.E.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 17
Shutthanandan, V.: IS-TuP2, 10
Smallwood, C.:
IS+SS+NS+BI+VT+MN+AS-WeA1, 15
Smyth, C.M.: 2D+EM+IS+MC+NS+SP+SS-WeA8, 13
Snezhkova, O.: IS+AS+SS-MoM11, 2

Somorjai, G.A.: IS+AS+SA+SS-WeM4, 11;
IS+AS+SS-MoM1, 1
Soukiasian, G.:
2D+EM+IS+NS+PS+SP+SS-FrM3, 17
Stach, E.: IS+AS+SS-TuA8, 8
Stine, R.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 17
Stolbov, S.: 2D+EM+IS+NS+PS+SP+SS-FrM6, 17
Stout, P.J.: IS+AS+SA+SS-MoA10, 5
Sui, X.: IS+AS+SA+SS-TuM13, 7;
IS+SS+NS+BI+VT+MN+AS-WeA3, 15;
IS+SS+NS+BI+VT+MN+AS-WeA4, 15

— T —

Takeda, S.: IS+AS+SS-TuA3, 8
Tallarida, N.: IS+AS+SA+SS-WeM3, 11
Tan, K.: IS+SS+NS+BI+VT+MN+AS-WeA10, 16;
IS+SS+NS+BI+VT+MN+AS-WeA9, 15
Tao, F.: IS+AS+SA+SS-MoA3, 4;
IS+AS+SA+SS-MoA8, 5;
IS+AS+SA+SS-WeM13, 12
Thevuthasan, S.A.: IS-TuP2, 10
Thissen, A.: IS+AS+SA+SS-MoA9, 5
Thonhauser, T.:
IS+SS+NS+BI+VT+MN+AS-WeA10, 16;
IS+SS+NS+BI+VT+MN+AS-WeA9, 15
Trotochaud, L.: IS+AS+SS-MoM5, 2
Tsoi, S.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 17
Tuailleon-Combes, J.: IS+AS+SS-MoM3, 1
Tyo, E.: IS+AS+SS-MoM3, 1

— U —

Unocic, R.R.: IS+AS+SS-TuA11, 9
Urpelainen, S.: IS+AS+SA+SS-MoA4, 4

— V —

Vajda, S.: IS+AS+SS-MoM3, 1
van Spronsen, M.A.: IS+AS+SS-MoM4, 1
Vijayakumar, M.: IS-TuP2, 10
Vishwanath, S.:
2D+EM+IS+MC+NS+SP+SS-WeA7, 13

— W —

Wallace, R.M.:
2D+EM+IS+MC+NS+SP+SS-WeA8, 13
Walton, S.G.: 2D+EM+IS+NS+PS+SP+SS-FrM1, 17
Wan, J.: 2D+EM+IS+MC+NS+SP+SS-WeA11, 14
Wang, H.: IS+SS+NS+BI+VT+MN+AS-WeA10, 16;
IS+SS+NS+BI+VT+MN+AS-WeA9, 15

Weatherup, R.S.: IS+AS+SS-MoM10, 2
Whitener, K.E.:
2D+EM+IS+NS+PS+SP+SS-FrM1, 17
Willman, J.T.:
2D+EM+IS+MC+NS+SP+SS-WeA1, 13
Winter, B.: IS+SS+NS+BI+VT+MN+AS-WeA7, 15
Wolf, M.: IS+AS+SA+SS-WeM2, 11
Wu, C.H.: IS+AS+SA+SS-WeM1, 11
Wu, Z.: IS+AS+SS-TuA9, 8

— X —

Xin, H.L.: IS+AS+SS-TuA8, 8
Xing, H.: 2D+EM+IS+MC+NS+SP+SS-WeA7, 13

— Y —

Yang, B.: IS+AS+SS-MoM3, 1
Yang, J.C.: IS+AS+SS-TuA8, 8; IS-TuP3, 10
Yano, J.: IS+AS+SA+SS-TuM3, 6
Yao, J.: IS+AS+SA+SS-TuM13, 7
Yazyev, O.V.:
2D+EM+IS+MC+NS+SP+SS-WeA3, 13
Yoshida, H.: IS+AS+SS-TuA3, 8
Yoshinobu, J.: IS+SS+NS+BI+VT+MN+AS-WeA12, 16
Yoshiomoto, S.:
IS+SS+NS+BI+VT+MN+AS-WeA12, 16
Yu, J.: IS+SS+NS+BI+VT+MN+AS-WeA4, 15
Yu, X.-Y.: IS+AS+SA+SS-TuM13, 7;
IS+SS+NS+BI+VT+MN+AS-WeA3, 15;
IS+SS+NS+BI+VT+MN+AS-WeA4, 15
Yu, Y.: IS+AS+SS-MoM5, 2

— Z —

Zhang, J.: IS+SS+NS+BI+VT+MN+AS-WeA4, 15
Zhang, L.: IS+AS+SS-TuA1, 8
Zhang, S.: IS+AS+SA+SS-MoA8, 5
Zhang, X.R.: 2D+EM+IS+NS+PS+SP+SS-FrM7, 17
Zhou, Y.: 2D+EM+IS+NS+PS+SP+SS-FrM2, 17; IS+AS+SA+SS-TuM13, 7;
IS+SS+NS+BI+VT+MN+AS-WeA3, 15;
IS+SS+NS+BI+VT+MN+AS-WeA4, 15
Zhu, H.: 2D+EM+IS+MC+NS+SP+SS-WeA8, 13
Zhu, Z.: IS+AS+SA+SS-TuM13, 7;
IS+SS+NS+BI+VT+MN+AS-WeA3, 15;
IS+SS+NS+BI+VT+MN+AS-WeA4, 15
Zinoviev, O.: IS+AS+SA+SS-WeM12, 12
Zuluaga, S.: IS+SS+NS+BI+VT+MN+AS-WeA10, 16;
IS+SS+NS+BI+VT+MN+AS-WeA9, 15