In-Situ and Operando Spectroscopy and Microscopy for Catalysts, Surfaces, & Materials Focus Topic
Room 101C - Session IS-ThA

Ambient Pressure Photoelectron Spectroscopy and Scanning Probe Techniques

Moderator: Xiao-Ying Yu, Pacific Northwest National Laboratory

2:20pm **IS-ThA1 The Influence of Oxygen on the Catalytic Interaction between CO$_2$ and Copper studied by High Pressure X-ray Photoelectron Spectroscopy**, *A. Regoutz, G. Kerherve, I. Villar-Garcia, C.K. Williams,* ***David Payne,*** Imperial College London, UK

CO$_2$ is a source for the production of carbon based fuels, such as methanol, and presents an attractive alternative to fossil fuels. Copper is an ideal catalyst for the reduction of CO$_2$, as it is able to direct reactions through stable intermediates, e.g. CO. An important question concerns the influence of oxygen on the catalytic activity and whether oxides are formed on the surface. As this system is an excellent material for the reduction of CO$_2$ a detailed understanding of the basis of its catalytic activity is essential and absolutely necessary for any further development.

X-ray photoelectron spectroscopy (XPS) is used widely in the solid-state sciences but due to its nature as an ultra high vacuum technique (pressure 10^{-9} mbar) it is not possible to study gas-solid interfaces. High-pressure XPS (HPXPS) is an advanced method which allows the measurement of solid samples at elevated pressures of between 1 and 30 mbar. This work presents results on the interaction of CO$_2$ and CO$_2$/O$_2$ with the surface of polycrystalline Cu followed by HPXPS. Cu 2*p* core levels, as well as the Cu L$_3$M$_{4,5}$M$_{4,5}$ Auger line are used to investigate the state of the Cu surface. The C 1*s* and O 1*s* core levels are used to track the interaction between CO$_2$/O$_2$ and Cu and are compared to CO$_2$/O$_2$ gas phase measurements.

Ultimately, the presented results provide a starting point for the detailed understanding of these catalysts and lead to the identification of possible ways to further improve and develop their properties.

2:40pm **IS-ThA2 Graphene Membranes for Atmospheric Pressure Photoelectron Spectroscopy**, ***Robert Weatherup****, B. Eren, Y. Hao, H. Bluhm, M.B. Salmeron,* Lawrence Berkeley National Laboratory (LBNL)

Determining the chemical state of a catalyst under realistic reaction conditions is of crucial importance in designing catalytic systems with improved activity and selectivity towards sought after products, and a key step in developing or improving existing industrial processes. Ambient pressure X-ray photoelectron spectroscopy APXPS has has proved a powerful technique for providing quantitative and surface sensitive (within a few nm) information on the chemical composition of surfaces/interfaces, with commercial analyzers available that allow measurements at pressure in the tens of mbar regime.[1] However numerous reactions of interest occur at atmospheric pressures and above, and thus the behavior observed in existing APXPS systems may not be truly representative of such reactions.

Here we demonstrate atmospheric pressure XPS using single-layer graphene membranes as photoelectron-transparent barriers that sustain pressure differences in excess of 6 orders of magnitude.[2] The graphene-based membranes are produced by transferring graphene grown by chemical vapor deposition,[3] onto metal (Au or Al) coated silicon nitride grids using a polymer-free transfer technique. The graphene serves as a support for catalyst nanoparticles under atmospheric pressure reaction conditions (up to 1.5 bar), where XPS allows the oxidation state of Cu nanoparticles and gas phase species to be simultaneously probed. We thereby observe that the Cu^{2+} oxidation state is stable in O$_2$ (1 bar) but is spontaneously reduced under vacuum. We further demonstrate the detection of various gas-phase species (Ar, CO, CO$_2$, N$_2$, O$_2$) in the pressure range 10–1500 mbar including species with low photoionization cross sections (He, H$_2$). Pressure-dependent changes in the apparent binding energies of gas-phase species are observed, attributable to changes in work function of the metal-coated grids supporting the graphene. We expect atmospheric pressure XPS based on this graphene membrane approach to be a valuable tool for studying nanoparticle catalysis.

[1] Starr, D. E.; Liu, Z.; Hävecker, M.; Knop-Gericke, A.; Bluhm, H. Investigation of Solid/vapor Interfaces Using Ambient Pressure X-Ray Photoelectron Spectroscopy. *Chem. Soc. Rev.***2013**, *42*, 5833–5857.

[2] Weatherup, R. S.; Eren, B.; Hao, Y.; Bluhm, H.; Salmeron, M. B. Graphene Membranes for Atmospheric Pressure Photoelectron Spectroscopy. *J. Phys. Chem. Lett.***2016**, *7*, 1622–1627.

[3] Hofmann, S.; Braeuninger-Weimer, P.; Weatherup, R. S. CVD-Enabled Graphene Manufacture and Technology. *J. Phys. Chem. Lett.***2015**, *6*, 2714–2721.

3:00pm **IS-ThA3 Development of Graphene Environmental Cells for Atmospheric Pressure Photoelectron Spectroscopy and Microscopy**, ***Andrei Kolmakov,*** Center for Nanoscale Science and Technology, NIST **INVITED**

Atmospheric pressure electron spectroscopy and microscopy are fast growing branches of the chemical and morphological analysis of the practically important interfaces relevant to catalysis, energy storage, harvesting and conversion as well as biomedical research. A great progress in this area achieved so far is largely due to meticulously engineered differentially pumped electron energy analyzers installed now at many laboratories and at synchrotron radiation facilities. Very recently a new approach for truly atmospheric pressure XPS, SEM, and TEM was demonstrated, which radically reduces the requirements to analytic instrumentation and, in principle, makes it possible high-pressure research using the standard laboratory electron spectrometers and microscopes. The core of this method are electron transparent membranes made of novel 2D materials, which separate high-pressure liquid (or gas) sample compartment from the UHV conditions of the spectrometer or microscope. In this report, we survey different designs and application practices of the graphene liquid cells and demonstrate their potential using X-ray Photoelectron Spectroscopy, X-ray Absorption Spectroscopy, Auger Electron Spectroscopy, Photoemission and Scanning Electron Microscopies of liquid interfaces.

4:00pm **IS-ThA6 Probing Surface Structural and Chemical Evolutions at Atomic Scale in Bi-metallic Catalysts using *In Situ* STEM**, ***Miaofang Chi,*** Oak Ridge National Laboratory*; C. Wang,* Johns Hopkins University*; K. More,* Oak Ridge National Laboratory*; Y. Xia,* Georgia Institute of Technology **INVITED**

The catalytic performance of nanocatalysts in terms of activity, selectivity, and durability, is primarily determined by the precise nature of the surface and near-surface atomic configurations. The surface atomic arrangements of nanoparticles (NPs), both in structure and chemistry, however, are highly dynamic during synthesis treatments and reaction conditions. Precisely understanding the complete evolution of NPs as a function of synthesis and reaction environments is imperative towards the rational design of nanocatalysts with optimized performance. With the ability of chemical-sensitive imaging at atomic resolution and the simultaneous acquisitions of electron energy loss spectroscopy (EELS) and energy dispersive X-ray (EDX) analysis, *in situ* scanning transmission electron microscopy (STEM) plays an important role in such studies. In this presentation, we will demonstrate how atomic-scale surface arrangements respond dynamically to *in situ* thermal annealing and gas reaction conditions in bi-metallic nanocatalysts. In particular, by tracking the *same individual* NPsduring *in situ* annealing, the influence of post-synthesis treatments on Pt$_3$Co NPs will be discussed. Five distinct stages of surface elemental rearrangements are discerned at the atomic scale: initial random (alloy) elemental distribution; surface Pt-skin-layer formation; nucleation of structurally ordered domains; ordered framework development; and finally, initiation of amorphization. Furthermore, the responses of surface atomic configurations in alloyed Pd-Au NPs to different reactive environments, including both reducing and oxidizing gases, will be discussed. In both cases, comprehensive interplays among phase evolution, surface faceting, and elemental inter-diffusion are revealed.

Acknowledgements: This work was supported by the Center for Nanophase Materials Sciences, which is U. S. Department of Energy Office of Science User Facility.

4:40pm **IS-ThA8 Calculations of Electron Inelastic Mean Free Paths for Liquid Water at Energies from 50 eV to 30 keV**, *H. Shinotsuka, B. Da, S. Tanuma, H. Yoshikawa,* National Institute for Materials Science (NIMS), Japan*;* ***Cedric Powell****, DR. Penn,* National Institute of Standards and Technology

We calculated electron inelastic mean free paths (IMFPs) for liquid water from its optical energy-loss function (ELF) for electron energies from 50 eV to 30 keV. These calculations were made with the relativistic full Penn algorithm (FPA) that has been used for previous IMFP and electron stopping-power calculations for many elemental solids [1]. We also calculated IMFPs of water with three additional algorithms: the relativistic single-pole approximation (SPA), the relativistic simplified SPA, and the relativistic extended Mermin method. These calculations were made using the same optical ELF in order to assess any differences of the IMFPs arising from choice of the algorithm. We found good agreement among the IMFPs from the four algorithms for energies over 300 eV. For energies less than 100 eV, however, large differences became apparent. IMFPs from the relativistic TPP-2M equation for predicting IMFPs were in good agreement with IMFPs from the four algorithms for energies between 300 eV and 30 keV but there was poorer agreement for lower energies. We made comparisons of our IMFPs with earlier calculations from authors who had used different algorithms and different ELF data sets. IMFP differences could then be analyzed in terms of the algorithms and the data sets. Finally, we compared our IMFPs with measurements of IMFPs and of a related quantity, the effective attenuation length (EAL). There were large variations in the measured IMFPs and EALs (as well as their dependence on electron energy). Further measurements are therefore required to establish consistent data sets and for more detailed comparisons with calculated IMFPs.

[1] H. Shinotsuka, S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. 47, 871 (2015).

5:00pm **IS-ThA9 Structural Response of Compact Copper Surfaces to CO Adsorption and its Effects of Reactivity***, **Baran Eren**, G.A. Somorjai, M.B. Salmeron,* Lawrence Berkeley National Laboratory (LBNL)

The most compact and stable surfaces of copper, namely the (111), (100), and (110) faces undergo massive reconstructions in the presence of carbon monoxide at room temperature at pressures in the Torr range. They decompose into two-dimensional nanoclusters. This is a double effect of of low cohesive energy of copper compared to other active metals and the high gain in adsorption energy at under-coordinated sites. With atomically resolved STM images and DFT calculations we provide a rationale for this behavior. Finally, we show that the surfaces which are broken up into clusters are more active for water dissociation, a key step in the water gas shift reaction.

5:20pm **IS-ThA10 Using a Novel In-situ/Operando Chemical Cell to investigate Surface Reactions such as the Reduction of Oxygen and Surface Oxides***, **Philipp Kerger**, D. Vogel, M. Rohwerder,* Max-Planck-Institut fuer Eisenforschung, Germany

A novel in-situ/operando electrochemical cell for doing Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) studies was developed. The cell allows treating the electrode surface with various preparation techniques such as sputtering and deposition as well as analyse it by XPS and other complementary characterisation methods. The electrode is covered under full electrochemical control by a nanoscopic electrolyte layer. This allows in-situ/operando investigations of electrochemical reactions such as oxygen reduction or oxide reduction by ambient pressure XPS. Examples will be presented and discussed in detail.

5:40pm **IS-ThA11 Monitoring of Electrochemical Reactions on Metal Surfaces with Sub-monolayer Sensitivity by Means of Polarization Optical Spectroscopy and EC-STM***, **Christoph Cobet**, M.-H. Chien, R. Sharif, V. Solokha, Gh. Barati, K. Hingerl,* Johannes Kepler University, Austria

We combine spectroscopic ellipsometry (SE), reflection anisotropy spectroscopy (RAS), and a homemade electrochemical scanning tunneling microscope (EC-STM) to study the surface of electrodes on the atomic level in liquids i.e. electrochemical environments. This combination of in-situ methods provides complementary information in comparison to conventional cyclic voltammetry (CV). While in CV the integrated charge and ion-exchange is measured, EC-STM provides direct snapshots of the surface morphology and electron corrugation. Polarization optical spectroscopy, on the other hand, is known for high surface/interface sensitivity regarding chemical modifications, sub-monolayer film formation and morphology transformations. The optical information can be additional recorded with almost the same time resolution like in conventional CV and allows the study of reaction kinetics. Thus it is finally possible to relate measured Faraday-currents to different surface processes.

Here, we report on the results on Cu single crystal surfaces of different orientation in halide solutions. The observed processes include halide adsorption, Cu(I) and Cu(II) dissolution, hydrogen evolution, as well as the initial formation of CuO. These studies are motivated by questions concerning e.g. the corrosion behavior and the catalytic functionality of Cu surfaces. The adsorption of Cl on Cu(110) at anodic potentials for example minimizes the surface energy by a formation of monoatomic steps parallel to the [001]-direction which finally ends up in a faceting of the surface. It turns out that some of the characteristic redox peaks in CV correlate with the surface transformation while others relate to a Cu(I) dissolution. The observed morphology transformations compares in parts with the oxide/chloride induced surface structures as measured UHV. This behavior is only observed at the more “open” and instable (110) surface. The (111) surface, in contrast, retains a smooth surface upon halide adsorption but with a distinct surface reconstruction. At more cathodic potentials we could monitor the hydrogen absorption and the hydrogen gas evolution at Cu surface by RAS and SE, respectively.

6:00pm **IS-ThA12 A Liquid-Jet AP-XPS Study of TiO_2 Nanoparticles in an Aqueous Electrolyte Solution***, **Randima Galhenage**, M.J. Makowski, J.M. Langford, J.C. Hemminger,* University of California, Irvine

To our knowledge, this is the first attempt to understand a true colloidal titania nanoparticle/water interface using Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS). Titania has attracted a significant amount of research interest due to its broad catalytic applications, many of which involve titania nanoparticles in aqueous solution. Therefore, understanding the titania nanoparticle/water interface is critical for the rational development of such systems. Here, we have employed liquid-jet Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) to investigate the solid/liquid interface of 20 nm diameter TiO_2 nanoparticles in 0.1M aqueous nitric acid solution. Liquid-jet AP-XPS experiments were conducted at beamline 11.0.2 of the Advanced Light Source at the Lawrence Berkeley National Laboratory. The temperature controlled liquid jet system generates a 25 um diameter liquid beam at a constant flow rate. The jet is irradiated by x-rays of variable photon energies which, therefore, enables us to probe different depths of the solution. Ejected electrons travel through a small aperture and are analyzed by a deferentially pumped electrostatic analyzer. A combination of the Ti2p line shape and the absolute binding energies of Ti2p and O1s reflect a stoichiometric titania lattice and no indication of oxygen vacancies (Ti^{3+}). Further, by increasing the x-ray excitation energy, the difference in O1s binding energies between that of liquid water ($O1s_{liq}$) and the titania lattice ($O1s_{lat}$) oxygen was measured over an increasing experimental probe depth into the particle. The titania lattice, $O1s_{lat}$, binding energy decreases by 250 meV when probing from the surface into the bulk of the particle. This binding energy difference cannot be accounted for by any other interfacial species as they should have a larger binding energy shifts with respect to the lattice oxygen. Moreover, due to the lack of characteristic Ti^{3+} signal, it is clear that further dissociation of water does not occur on the colloidal particles during the course of our XPS study. The observed change in binding energy is interpreted as downward band bending at the surface, resulting from accumulated charge on the surface of the titania nanoparticle.

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