Biomaterial Interfaces Division
Room 318 - Session BI+AS+HC+SS-MoA
Bioinspired Materials and Applications

Moderators: Sally M. McArthur, Deakin University, Australia, **Tobias Weidner**, Aarhus University, Denmark

1:40pm **BI+AS+HC+SS-MoA-1 Bioinspired Approaches to Prevent Microbes and Fouling on the Surface of Membranes***, R. Shah, T. Goodwin,* ***Jessica Schiffman,*** University of Massachusetts Amherst **INVITED**

The reliability and ease of operation of membrane-based water purification systems has led to their increased use in water and wastewater treatment. However, water and energy are mutually dependent critical resources; to produce clean water requires energy and the production of energy requires large volumes of water. Unfortunately, when microorganisms and other foulants accumulate on the surface of membranes and block their pores, more energy is required to operate the separation process even though its productivity is significantly reduced. The overall goal of this talk is to illustrate how bioinspired approaches can be used to enhance the properties of ultrafiltration membranes. Our first approach will demonstrate how we controlled the deposition of the bioinspired “glue” dopamine in order to fabricate ultrafiltration membranes with retained selectivity and pure water flux. Molecules for polymerization were immobilized on the membrane’s surface yet prevented from attaching to the membrane’s pores due to a backflow of nitrogen gas achieved using simple in-house constructed equipment. If time allows, I will provide an overview of our recent exploration into how pitcher plant inspired immobilized liquids can dramatically increase the fouling resistance of membranes that have consistent flux over at least ten cycles of operation. Biofouling during membrane-based operations is a major challenge and we suggest that there are numerous bioinspired approaches that can address this problem.

2:20pm **BI+AS+HC+SS-MoA-3 Antibiotic-Free Liquid Layers Decrease Bacterial Adhesion on Catheters In Vivo***, C. Fong,* University of Maine*; M. Andersen, A. Flores Mireles,* Notre Dame*;* ***Caitlin Howell,*** 5737 Jenness Hall

The rise of antibiotic resistance is one of the greatest global public health challenges of our time. Although new antibiotics continue to be discovered, the pace is slowing while the rate of discovery of new antibiotic-resistant organisms continue to grow at an alarming rate. New, non-chemical approaches are needed which can reduce bacterial surface attachment and growth without leading to further resistance. Over millions of years, Nature has developed several ways to mechanically direct or stop bacterial growth, leading to materials-based antibacterial mechanisms which are elegant, effective, and difficult for bacteria to overcome. One of these approaches, immobilized liquid layers, functions via the use of a mobile, dynamic, and sacrificial physical barrier between the bacteria and the surface which they may contaminate. *In vitro* proof-of-concept experiments using urinary catheters— one of the most common and infection-prone medical devices—liquid layers were found to reduce bacterial adhesion by 99% compared to untreated controls. In tests *in vivo*, the system performed beyond expectations, reducing not only bacterial adhesion but overall surface protein contamination as well. The results provide hope that continuing to engineer materials-based approaches to stop bacterial adhesion and growth can help us to stay ahead of antibiotic resistance.

2:40pm **BI+AS+HC+SS-MoA-4 Discovery of Cell Instructive Materials for Next Generation Medical Devices: Exploring Microtopography and 3D Shapes***,* ***Morgan Alexander,*** University of Nottingham, UK

The polymer biomaterials found in the clinic today are dominated by materials that have been chosen largely on the basis of their availability and mechanical properties. It would be desirable to design our way forward from this situation to new and better biomaterials chosen for positive interactions with surrounding cells and tissues. Unfortunately, our understanding of the interface between most materials and biology is poor. Only in isolated cases is there a good understanding of cell-material surface interactions and fewer still where material-tissue interactions are well characterised and understood.

This paucity of information on the mechanism of biomaterial interactions within the body acts as a roadblock to rational design. Consequently, we have taken a high throughput screening approach to discover new bio-instructive polymers from large chemical libraries of synthetic monomers presented as micro arrays. [1,2] This approach, akin to engineering serendipitous discovery, has resulted in novel materials which we have taken all the way from the lab to the clinic.

More recently we have extended our approach to explore the opportunities offered by micro topography and 3D shape manipulation to provide bio-instructive cues topography to immune cells, stromal cells and pathogenic bacterial cells. To do this we have developed and adopted a range of high throughput screening platforms, including theTopoChip[3], ChemoTopoChip [4] and used 3D printing to produce the ArchiChip [5]. The talk will focus on these topographic platforms and our findings, in particular novel topographies that reduce bacterial biofilm formation and provide beneficial host cell responses which has the potential to reduce infection in medical device implantation.[6]

References

[1] Combinatorial discovery of polymers resistant to bacterial attachment Hook et al. **Nature Biotechnology** 30 (9), 868-875 (2012).

[2] Materials for stem cell factories of the future Celiz et al. **Nature Materials** 13 (6), 570-579 (2014).

[3] Immune modulation by design: using topography to control human monocyte attachment and macrophage differentiation Vassey et al. **Advanced Science** 7 (11), 1903392 (2020).

[4] Discovery of synergistic material-topography combinations to achieve immunomodulatory osteoinductive biomaterials using a novel in vitro screening method: The ChemoTopoChip Burroughs et al. **Biomaterials** 271, 120740 (2021).

[5] Innate Immune Cell Instruction Using Micron-scale 3D Objects of Varied Architecture and Polymer Chemistry: The ChemoArchiChip Vassey et al. under review.

[6] Micro topographical instruction of bacterial attachment, biofilm formation and in vivo host response Romero et al. under review.

3:00pm **BI+AS+HC+SS-MoA-5 Development of a Method for Visualizing Nanometer-Scale Three-Dimensional Structures of Chromosomes by Three-Dimensional Atomic Force Microscopy***,* ***Ryohei Kojima****, K. Miyazawa, K. Teramae,* Kanazawa University, Japan*; T. Sumikama,* PRESTO, JST, Japan*; M. Meguro,* Research Center for Experimental Modeling of Human Disease, Kanazawa University, Japan*; K. Imadate,* Osaka University, Japan*; N. Okano,* Kanazawa Unversity, Japan*; S. Horike,* Research Center for Experimental Modeling of Human Disease, Kanazawa University, Japan*; K. Hirahara,* Osaka University, Japan*; T. Fukuma,* Kanazawa University, Japan

Three-dimensional atomic force microscopy (3D-AFM) is capable of obtaining 3D force images at solid-fluid interface in sub-nanometer scale. In the previous research, 3D-AFM visualized molecular-scale hydration and flex molecular structures of bio samples such as lipid and DNA. As a next step, it is required to visualize 3D complex structures with high order molecular organizations.

In this research, we developed 3D-AFM for visualizing 3D folded structures of human chromosomes. Chromosome (Fig. 1a) is composed of 3D folded structures that has important roles for genetic transfer. However, nanometer-scale 3D folded structures of human chromosomes have not been well understood yet. It is expected that 3D-AFM contributes to chromosome study, but it is difficult to measure inside of 3D folded structures of chromosomes by conventional conical tip without damage of samples by tip scanning. To visualize 3D folded structures of chromosome by 3D-AFM, we fabricated a carbon nanotube (CNT) tip (length > 500 nm, diameter < 20 nm) to penetrate chromosomes by 3D-AFM. By using the conventional tip and home-made CNT tip (Fig. 1c(i)-d(i)), we performed 3D-AFM of human chromosomes, and obtained 3D frequency shift (Δf) image (Fig. 1b). We extracted single Δf curves from the 3D Δf images obtained with Si tip and CNT tip, respectively (Fig. 1c(ii)-d(ii)). Δf curve using CNT tip shows oscillatory profile until 500 nm in depth from the surface of the chromosome in contrast to the Δf curve using Si tip. This result suggests that the obtained 3D Δf image using CNT tip reflects structures inside chromosome. Based on this research, applications of 3D-AFM will be expanded for visualizing 3D structures of biological samples in various research fields.

3:20pm **BI+AS+HC+SS-MoA-6 Mass-Manufactured Surface Textures Kill Bacteria as Part of Low-Cost Water Purification Devices***, **Liza White**, C. Howell,* University of Maine

Water purification and disinfection, particularly of turbid water, is a significant and growing need worldwide. Pulsed electric field (PEF) devices can be used to inactivate pathogens in water; however, manufacturability, power consumption, cost, and portability remain significant hurdles. Through leveraging paper industry technology in Maine, we have optimized electric field generation using custom textured film in a roll-to-roll manufacturing process to act as the functional part of portable PEF water purification devices. Specifically, we used commercially produced textured release paper as a substrate for the film electrodes and explored different types of metal coating to reduce the overall power consumption, cost, and manufacturability. CAD and modeling software was then used to simulate various textures to determine the optimal texture to focus the electric field while keeping a low total current density, and a custom texture was designed. The mass-manufactured textured materials were cut into singular flow cells and were sputter-coated with various metals and assembled. The flow cells were connected to a pulsed generator that pulsed a square wave at 15 µs at a frequency of 100 Hz with a voltage of 100 V. Water with a known concentration of bacteria was pushed through the flow cells at a rate of 200 µL/minute. The outlet sample was collected, and bacterial reduction was calculated. These tests demonstrated that mass-manufactured surface textures could function as part of a low-cost PEF water purification device. The development of low-cost PEF water purification devices based on surface texture will help provide more accessible clean water in the face of growing water shortages.

4:00pm **BI+AS+HC+SS-MoA-8 Nature-inspired Materials for Energy and Environmental Sustainability***, **Tak Sing Wong**,* The Pennsylvania State University **INVITED**

With an evolutionary history of 3.95 billion years and over 8 million species on earth, natural organisms have often served as blueprints for the design of highly functional engineered materials. In particular, natural species have demonstrated how different micro/nanoscale surface architectures can yield an array of distinct interfacial functions. Understanding the fundamental principles behind these natural surfaces will aid the design of multifunctional materials for a range of energy and sustainability applications. In this talk, I will discuss a number of specific examples showcasing our recent biologically inspired technologies which take inspirations from insects to plants. These examples include the development of anti-fouling and self-cleaning surfaces inspired by the slippery rims of the *Nepenthes* pitcher plants, as well as the fabrication of ultra-antireflective coatings inspired by the leafhopper-produced brochosomes. Perspectives on how nature-inspired materials may impact future applications in energy and sustainability will be discussed.

4:40pm **BI+AS+HC+SS-MoA-10 Programmable Biomimetic Light-Harvesting Systems: Quantum-Optical Control of Light-Matter Interactions***, A. Lishchuk, E. Csanyi, **Graham Leggett**,* University of Sheffield, UK

The absorption of light by molecules leads to the formation of excitons (electron-hole pairs). Control of excitons is essential for many new and emerging technologies, but the inefficient dynamics and short diffusion lengths (~ 10 nm) of excitons in molecular systems limit their utilisation.Theory suggests that exciton diffusion lengths could be enhanced by several orders of magnitude in the strong light-matter coupling regime. However, design principles for the production of photonic materials that exploit strong coupling are lacking. We have found that photosynthetic light-harvesting complexes (LHCs) from plants and bacteria are strongly coupled to localised surface plasmon resonances (LSPRs) in arrays of metal nanostructures, yielding macroscopically extended excited states that enable coherent, non-local excitation transfer and the creation of bespoke optical states not found under weak coupling. However, proteins are not suitable for putative applications of molecular photonic materials. Inspired by photosynthetic LHCs, we demonstrate the fabrication of programmable plexcitonic antenna complexes, in which polymer scaffolds organise excitons within localised surface plasmon resonances to achieve strong light-matter coupling, yielding delocalised excited states (plexcitons) that extend across at least 1000s of pigments. In our plexcitonic antenna complexes, poly(amino acid methacrylate) scaffolds grown from gold nanostructures by atom-transfer radical polymerisation (ATRP) organise excitons (transitions in chlorophylls) within LSPRs to achieve strong light-matter coupling, yielding Rabi energies up to twice as large as those achieved with biological LHCs. The energies of the resulting delocalised excited states (plexcitons) are programmed by varying the degree of polymerisation, scaffold packing density and chlorophyll loading. Steric hinderance in fully-dense PCysMA brushes limits binding of bulky chlorophylls, but the chlorophyll concentration can be increased to ~2M, exceeding that in biological light-harvesting complexes, by controlling the grafting density and polymerisation time. Moreover, synthetic plexcitonic antenna complexes display pH and temperature responsiveness, facilitating active control of strong plasmon-exciton coupling. These biologically-inspired metamaterials offer great promise for the design of new types of molecular photonic device.

5:00pm **BI+AS+HC+SS-MoA-11 Microfluidic QCM with Ultrahigh Q-Factor: A New Paradigm for Acoustic Biosensing?***, Y. Zhao,* Duke University*; Z. Parlak,* Qatch LLC.*; M. Yu,* Duke University*; D. French,* Qatch LLC.*; W. Aquino, **Stefan Zauscher**,* Duke University

Acoustic thickness shear mode transducers, such as the quartz crystal microbalance (QCM), can provide high throughput biomolecular detection for diagnostics with minimal sample preparation. A QCM's resonance frequency change (Δf) is generally related to the mass change (Δm) due to analyte binding on the sensor surface. If equipped with dissipation monitoring, a QCM's dissipation (D or ΔD) is related to the viscoelastic properties of the surface-bound analyte. Although current QCM sensors are simple and robust devices, they generally require high sample volumes and suffer from low sensitivity/resolution due to fluid damping.

We show that by adding microfluidic channels onto QCM sensors, we can strongly couple small amounts of liquid within the channels to the sensor, thereby largely eliminating fluid damping. This coupling eliminates dissipation effects during shear excitation and thus dramatically increases the quality factor (Q-factor) of the sensor and allows for accurate measurement of changes in fluid density, and therefore also for biomolecular mass measurements in liquid environments.

The abrogation of damping effects arises from the almost lossless coupling of the liquid to the side walls of the channels, which results in an in-plane pressure wave. We found that if the wavelength of the pressure wave is considerably longer than the channel width, the liquid inside the channels is strongly coupled to the channel walls and thus damping is suppressed. Since viscous effects are largely eliminated, the microfluidic QCM (µ-QCM) is also insensitive to temperature-induced viscosity changes. With a high Q-factor, direct data interpretation, pure mass sensitivity and temperature insensitivity, and small device size, the µ-QCM provides a new paradigm for acoustic biosensing.

We used Finite Element Analysis (FEA) to test our hypothesis that the in-plane pressure wave generated by the channel side walls is responsible for the enhanced performance of the µ-QCM. Furthermore, we conducted a nondimensional analysis to reveal the most important parameters, including channel dimensions, crystal thickness, and fluid viscosity/density, and how they affect the dissipation. This knowledge can be easily extended to other acoustic bio-transducers to improve their sensitivity/resolution.

Finally, we show the design and microfabrication of µ-QCM devices, and their testing with a range of liquids with known viscosity and density, to demonstrate the high Q-factor of µ-QCMs and to demonstrate the latter's ability to sense density changes (unencumbered by viscosity) in small (~nL) sample volumes.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-MoA

Advances in Materials and Analysis in Heterogeneous Catalysis I

Moderators: Dan Killelea, Loyola University Chicago, **Swetlana Schauermann**, Christian-Albrechts-University Kiel, Germany

2:00pm **HC+AS+SS-MoA-2 Electrocatalytic Activity of Size-Selected Sub-Nano Pt Clusters Toward the Hydrogen Evolution Reaction***, **Tsugunosuke Masubuchi**,* University of Utah*; S. Kumari, Z. Zhang, P. Sautet, A. Alexandrova,* University of California at Los Angeles*; H. White, S. Anderson,* University of Utah

Platinum is known to exhibit high electrocatalytic activity toward the hydrogen evolution reaction (HER). From a sustainable point of view, sub-nano Pt clusters can be promising HER electrocatalysts because their electrochemically active surface area per mass is much larger than that of bulk Pt or larger Pt nanoparticles. There are fundamental questions, however, about the nature of the HER mechanism, including the electronic and structural properties of the catalytic sites required.

To this end, we studied the HER activity of atomically size-selected sub-nano Pt clusters deposited on conductive oxide supports. The electrodes of sub-nano Pt clusters were prepared using a home-built cluster beam deposition instrument, which consists of a laser vaporization cluster source, a mass-selecting ion beamline, and an ultrahigh vacuum (UHV) end station for cluster deposition. The oxide substrates were cleaned in advance by Ar^+ sputtering and annealing and tested to ensure that they are electrochemically inactive. Ions of size-selected sub-nano Pt clusters were deposited on the substrates until a certain coverage was reached. The sample electrodes prepared in this way were exposed to an O_2-free $HClO_4$ electrolyte solution, and electrochemical measurements were performed.

In this contribution, we will discuss how every Pt atom counts for the HER activity of size-selected sub-nano Pt clusters. We will particularly show that by the interplay between the experiment and quantum chemical calculations, certain Pt clusters, composed of only several atoms, can reduce protons and adsorb hydrogen atoms very efficiently, which leads to their superior HER activity.

2:20pm **HC+AS+SS-MoA-3 In situ X-ray Absorption Spectroscopy to Probe the Dynamics of Ni_3Fe catalysts: Implications for Dry Methane Reforming***, L. Cruz,* University of California, Riverside*; J. Hong,* Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory*; S. Shah,* University of California - Riverside*; S. Bare,* Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory*; **Kandis Leslie Gilliard-AbdulAziz,*** University of California - Riverside **INVITED**

The exsolution of nanoparticles from perovskite precursors has been explored as a route to synthesize firmly anchored catalysts. The characteristics of these exsolved nanoparticles, such as size, composition, and morphology, are highly dynamic depending on the redox nature of the reactive environment. Their dynamic nature warrants a study that tracks the changes with in-situ and ex-situ characterization to benchmark states. In this talk, we will discuss the use of operando X-ray Absorption Spectroscopy (XAS) to study the formation, evolution, and regeneration of exsolved NiFe nanoparticles from $LaFe_{0.8}Ni_{0.2}O_3$ perovskite oxide precursors. STEM-HAADF with EDS analysis was used to measure the nanoparticle composition and morphology after exposure to dry methane reforming (CH_4, CO_2, CO, H_2, H_2O), reductive (H_2) or oxidative (O_2) conditions. Our findings show that the nanoparticle formation in 5%H_2/He occurs in sequential exsolution mechanisms where Ni exsolves first and then Fe. During DRM conditions, the Ni composition transforms from predominantly Fe-rich to Ni-rich NiFe catalysts. Lastly, we will discuss the regeneration of bimetallic alloys and implications for future work in exsolved bimetallic alloys.

3:00pm **HC+AS+SS-MoA-5 Photocatalysis between High-Purity and Applied Reaction Conditions: Understanding Carbon Dioxide Reduction on the Molecular Level***, **Jennifer Strunk,*** Leibniz Institute for Catalysis, Germany **INVITED**

Reducing carbon dioxide just with the energy of (sun)light to platform chemicals for the chemical industry (e.g. carbon monoxide, methane) is still a highly desirable process to enable a recycling of this greenhouse gas. Yet, despite more than 40 years of research, the achievable yields in photocatalytic carbon dioxide reduction have not increased significantly, thereby clearly failing to meet demands for industrial implementation. One significant hurdle is our limited understanding of the chemical processes on the molecular scale, in particular under reaction conditions relevant to a future application. This is to a large extent due to the vastly different, and in part badly described, reaction conditions applied in published works, making it practically impossible to compare the different studies.

Our approach is the design of a reactor and a research methodology to enable highly reproducible studies in photocatalytic carbon dioxide reduction. Using solely construction parts suitable for high vacuum applications, we have developed the so-called “high-purity gas-phase photoreactor” with gas chromatographic trace gas analysis, allowing to obtain reproducible results on the ppm level. It can also function as bridge between true single-crystal studies and possible reaction conditions in practical applications.

Using this device, fair comparisons of different photocatalysts suggested in literature has been possible. This revealed the well-known titanium dioxide as one of the best materials, despite its large bandgap. Reliable apparent quantum yields have been determined. Focusing our studies on titania, it has been possible to obtain a rather complete picture of the reaction progress on the molecular scale. The reaction from carbon dioxide to methane is likely not a linear sequence of reduction steps but involves also oxidative steps by a reaction with holes. Even if methane as one-carbon product is formed, intermediates involving a C-C bond are involved. The limiting step is the water oxidation reaction, which does not run to completion. Instead, oxygen-related species are stored on or in titania until the material is saturated and the reaction ceases. These findings indicate that (i) completely other materials, possibly Z scheme systems with suitable cocatalysts, need to be developed that allow a less complex surface reaction pathway, and (ii) that (biogenic) methane may be a better co-reactant than water in a “photo dry reforming” reaction.

4:00pm **HC+AS+SS-MoA-8 Electrocatalytic Nitrate Reduction: Controlling Adsorbate Affinity to Tailor Reaction Products***, **Kelsey Stoerzinger,*** Oregon State University **INVITED**

The electrochemical nitrate reduction reaction (NO_3RR) represents a distributed approach for water treatment and chemical synthesis (ammonia) as an alternative to conventional carbon-intensive processes (Haber-Bosch). Catalysts requirements for this reaction, however, are immense: water/protons are required to reduce nitrate but compete with NO_3RR to evolve hydrogen gas at comparable potentials, and selectivity along an 8 e^-/10 h^+ process is required to produce ammonium. Here we investigate NO_3RR activity and ammonium selectivity across 3d and select 4d transition metals in neutral conditions prototypical of nitrate-containing source waters, developing fundamental understanding of the competitive processes that give rise to these trends to guide future catalyst design. We develop a microkinetic model capturing the potential-dependent nitrate rate order, arising from competitive adsorption between nitrate and hydrogen. Competition with the hydrogen evolution reaction is manifest in the NO_3RR Faradaic efficiency, described by catalyst work function. Selectivity to ammonium nominally increases as transition metal d-band center energy approaches and overcomes the Fermi level, with Co representing an optimal catalyst. Density functional theory calculations identify a Sabatier-like relationship between ammonium selectivity and the driving forces for nitrite reduction to nitric oxide and the dissociation of nitric oxide, where Co represents a local optimum between these two processes. These results identify competing design considerations – linking electronic structure to mechanistic selectivity-limiting steps – offering strategies to improve existing catalysts and design new alloy compositions for NO_3RR to ammonium.

4:40pm **HC+AS+SS-MoA-10 Energetics and Growth Modes of Ni and Pd Nanoparticles on Graphene / Ni(111)***, **Kun Zhao**, J. Rumptz, N. Janulaitis, C. Campbell,* University of Washington

The use of carbon supports for late transition metal nanoparticle catalysts has grown substantially in recent years due to efforts to develop electrocatalysts for clean energy applications and catalysts for new aqueous-phase biomass-related conversions, and due to the evolution of new carbon materials with unique properties (e.g., graphene, carbon nanotubes, etc.). However, much less is known about the bonding energetics of catalytic metal nanoparticles on carbon supports in comparison with oxide supports, which are more common for thermal catalysis. Here we investigated the growth morphologies and heats of adsorption of Ni and Pd vapor deposited onto graphene/Ni(111) at 300 K and 100 K using He^+ low-energy ion scattering (LEIS) and single crystal adsorption calorimetry (SCAC). For Ni/graphene/Ni(111), the SCAC results showed at 300 K the heat of adsorption of Ni vapor increases rapidly from 336 kJ/mol initially to the heat of sublimation (430 kJ/mol) by 2 ML, and at 100 K from 230 kJ/mol to the heat of sublimation slower by 3.5 ML. The growth models derived from LEIS results suggested that Ni grows as flat-topped islands with a thickness of ~1.5 nm when deposited at 300 K, and small hemispherical cap shape with a number density of 2×10^{16} particles/m^2 when deposited at 100 K. The particle size and morphology account for the differences in the heat of adsorption versus coverage at these two temperatures. The Ni chemical potential as a function of average particle diameter in the 0.5 to 4 nm range at 100 K was determined from the LEIS and SCAC measurements, and an adhesion energy of 3.6 J/m^2 was determined from fitting the chemical potential vs diameter to a theoretical model. For Pd/graphene/Ni(111), the heats of adsorption of Pd increase with coverage similarly to Ni at 300 K and 100 K and reach the heat of sublimation (370 kJ/mol) by 2.8 ML, with an initial heat of adsorption at 300 K (272 kJ/mol) that is 47 kJ/mol higher than at 100 K. The trends in the heat of adsorption are supported by the growth model from the LEIS results. Similar to Ni growth, however with much smaller particle size and larger particle density, Pd grows as flat-topped islands at 300 K with a thickness of ~0.85 nm, and hemispherical cap shape at 100 K with a number density of 6×10^{16} particles/m^2. The evolution of Pd chemical potential along with particle size was determined in the average particle diameter range of 0.6 – 2.5 nm at 100 K and the adhesion energy was found to be 3.8 J/m^2.

5:00pm **HC+AS+SS-MoA-11 Size Dependent CO$_2$ Reduction Activity and Selectivity of Ag Nanoparticle Electrocatalysts in sub-5 nm Regime***, **Xingyi Deng**,* NETL/LRST*; D. Alfonso,* NETL*; T. Nguyen-Phan,* NETL/LRST*; D. Kauffman,* NETL

Coinage metals (Au, Cu and Ag) are state-of-the-art electrocatalysts for the CO$_2$ reduction reaction (CO$_2$RR). Size-dependent CO$_2$RR activity of Au and Cu has been studied, and increased H$_2$ evolution reaction (HER) activity is expected for small catalyst particles with high population of undercoordinated corner sites. A similar level of consensus is lacking for Ag catalysts because the ligands, capping agents, or stabilizers typically used to control particle size and crystallographic orientation can block specific active sites and mask inherent activity trends. We used a combination of ultrahigh vacuum surface science techniques, electrochemical measurements, density functional theory, and microkinetic modeling to finely resolve the size dependent CO$_2$RR activity and selectivity of Ag nanoparticle electrocatalysts in the sub-5 nm range. Experimental results identified CO$_2$RR selectivity increased with average particle diameter between 2 to 6 nm with 3.7 ± 0.7 nm diameter Ag particles demonstrating the highest combination of CO$_2$RR activity and selectivity. A nearly identical size-dependent trend was also predicted in computational modeling: smaller diameter particles favored H$_2$ evolution reaction (HER) due to a high population of Ag edge sites, whereas larger diameter particles favored CO$_2$RR as the population of Ag(100) surface sites grew. Our results resolve the CO$_2$RR behavior of Ag in the crucial sub-5 nm range and establish an effective minimum size limit for balancing activity and selectivity. Particles below a critical diameter suffered from poor selectivity, while larger particles above the critical diameter demonstrated bulk-like activity that led to reduced catalyst utilization. These results provide insight into the size-dependent CO$_2$RR activity of pristine Ag catalysts and will help guide future catalyst development efforts.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 321 - Session HC+AS+SS-TuM
Energetic Processes and Tailored Surfaces in Heterogeneous Catalysis

Moderators: Tim Schäfer, Georg-August Universität, Göttingen, Germany, **Arthur Utz**, Tufts University

8:40am **HC+AS+SS-TuM-3 Adsorption and Reaction of Acetic Acid on Single-Crystal and Faceted Nanoparticle Anatase $TiO_2(101)$ Surfaces***, C. O'Connor, R. Ma, Y. Wu, W. DeBenedetti, F. Gao, Y. Wang, G. Kimmel, **Zdenek Dohnálek**,* Pacific Northwest National Laboratory

Understanding the adsorption and reactivity of carboxylic acids on anatase TiO_2 is of great interest in catalysis for the potential synthesis of selective carbon-coupling reaction products. A comparative investigation of the adsorption and reaction of acetic acid on single-crystal planar and faceted nanoparticle anatase $TiO_2(101)$ surfaces was performed using a combination of infrared spectroscopy, temperature-programmed reaction spectroscopy and scanning tunneling microscopy. Acetic acid adsorbs as bidentate acetate and monodentate acetic acid dependent on the adsorption temperature as determined by infrared spectroscopy and scanning tunnelling microscopy measurements on single-crystal TiO_2 under ultra-high vacuum conditions. The adsorption of bidentate acetate has a saturation coverage of 0.5 ML. However, high-density phases containing a mixture of bidentate acetate and monodentate acetic acid and solely monodentate acetic acid occur at low temperature conditions. The sole presence of bidentate acetate is observed at elevated temperature due to the facile conversion of monodentate acetic acid to bidentate acetate and desorption of monodentate acetic acid which precludes investigating the reactivity of high-density phases under vacuum conditions. The presence of monodentate acetic acid persists to notably higher temperatures on the faceted nanoparticles than single-crystal TiO_2. The reaction of bidentate acetate produces ketene and water as determined by temperature-programmed reaction spectroscopy on single-crystal TiO_2. Notably, there is an absence of carbon-carbon coupled products, such as acetone, from the sole reaction of bidentate acetate. The selectivity of bidentate acetate is independent of coverage up to the saturation coverage. Similarly, the reaction of acetic acid on faceted nanoparticle TiO_2 produces predominantly ketene and water as determined by temperature-programmed reaction spectroscopy under low vacuum conditions. This study provides mechanistic insight into the reactivity and stability of surface-bound intermediates that are present for the reaction of acetic acid on anatase TiO_2 catalysts.

9:00am **HC+AS+SS-TuM-4 Phase Transformation of Single Micro-Sized TiO_2 Crystals***, W. Lu, H. Zhu, N. Craft, K. Park, **Zhenrong Zhang**,* Baylor University

Understanding the reactivity of various crystal faces in different polymorphs of TiO_2 in photoreaction is important for many photocatalytic applications. Here, we monitored and studied the anatase-rutile phase transition (ART) processes of individual micro-sized TiO_2 crystals from the pure anatase phase to the mixed-phase, then to the rutile phase. High-quality micro-sized anatase TiO_2 crystals with a large percentage of (001) facets were hydrothermally synthesized. Micro-Raman spectroscopy mapping and scanning electron microscope (SEM) images were obtained at different annealing stages to correlate the crystal structure transformation with the morphology change. The ART processes of individual anatase particles are distinctive and depend on the various defects which serve as rutile nucleation sites. Two types of transition pathways are observed. In one type of growth pathway, rutile nucleation was formed at a corner of an anatase crystal. The rutile phase then gradually propagated over the rest part of the microparticle. The phase concentration calculated from Raman spectra revealed that the ART transition follows the first-order reaction mechanism. In the other type of growth pathway, multiple rutile nucleation sites formed simultaneously on different edges and corners of the microcrystal. The rutile phase then spreads over the whole crystal from these nucleation sites forming multi-grain crystals.

9:20am **HC+AS+SS-TuM-5 Reactivity of Formic Acid on Single Atom Rh Supported on $Fe_3O_4(001)$***, **Christopher Lee**, M. Sharp, S. Smith, B. Kay, Z. Dohnálek,* Pacific Northwest National Laboratory

Single-atom catalysis is a growing area of research due to the potential to qualitatively transform the activity and selectivity of supported metal catalysts. However, the fundamental surface science studies of their unique properties have not been widely studied. Here we investigate the reactivity of formic acid on several model Rh catalysts, including single Rh adatoms, Rh incorporated into the support oxide lattice, and metallic Rh clusters on $Fe_3O_4(001)$ under ultrahigh vacuum conditions. The single Rh adatoms are found to be the most active towards CO_2 production, followed by incorporated Rh and then by Rh nanoclusters. While the reaction of formic acid with $Fe_3O_4(001)$ primarily results in CO desorption at ~570 K, the addition of small amounts of single adatom Rh (~0.01 Rh per $Fe_3O_4(001)$ unit cell (u.c.)) results in a dramatic shift towards CO_2 production at lower temperatures starting at 540 K and dropping to ~470 K at larger HCOOH coverages. The incorporated Rh system also yields CO_2 product, but it takes ~15-20 times as much Rh to achieve the same activity as the Rh adatoms. Rh nanoclusters exhibit reactivity similar to metallic Rh with low-temperature CO_2 and H_2 desorption at ~310 K while still producing substantial amounts of CO_2 at 450-500 K, not observed on pure $Fe_3O_4(001)$. These differences demonstrate that different forms of Rh supported on $Fe_3O_4(001)$ affect the reactivity of the catalytic surface beyond the local stabilized transition metal site. The stabilized adatoms turn over multiple adsorbates to products demonstrating the importance of spillover from the support oxide. Furthermore, the single Rh adatoms and incorporated Rh exhibit an intermediate activity distinct from metallic Rh nanoparticles or the $Fe_3O_4(001)$ substrate, demonstrating the additional degree of reactive tuning provided by single-atom catalysts. The similarity in reactive behavior between the Rh adatom and mixed Rh oxide systems hints toward a common mechanism between the systems. The much larger reactivity of the Rh adatom system suggests that under reaction conditions, a small amount of the mixed Rh oxide may be dynamically converted to Rh adatom and that the Rh adatom is responsible for the lower temperature CO_2 activity.

9:40am **HC+AS+SS-TuM-6 WO_3/Ag_2S type-II Hierarchical Heterojunction for Improved Charge Carrier Separation and Photoelectrochemical Water Splitting Performance***, **Jyoti Yadav**, J. Singh,* IIT DELHI, India

In the present work, WO_3/Ag_2S heterojunction was fabricated to achieve an improved photoelectrochemical (PEC) water splitting performance. To prepare the working electrodes,a two step method was adopted which includes, a thin film of WO_3 deposited using DC sputtering and a well-separated Ag_2S nanorods fabricated by glancing angle deposition,. The PEC response was studied for bare WO_3, Ag_2S, and WO_3/Ag_2S heterojunction. The as-prepared WO_3/Ag_2S heterojunction samples revealed higher absorption as well as higher photocurrent density of 2.40 mA/cm^2 (at 1V Ag/AgCl) as compared to bare WO_3 thin film (0.34 mA/cm^2). The enhancement in the photocurrent density of WO_3/Ag_2S electrodes could be ascribed to the formation of the type-II heterojunction between WO_3 and Ag_2S which effectively separates and transfers the charge carriers at the interface. In addition, increased trapping of light due to vertically tilted Ag_2S nanorods structures results in an effective absorption of light. Furthermore, electrochemical impedance spectra measurements showed that WO_3/Ag_2S samples have lower charge transfer resistance at the semiconductor electrolyte interface with high flat band potential. The present work provides a deeper insight on the role of the interface formed between WO_3 and Ag_2S for the photoelectrochemical water splitting response.

11:00am **HC+AS+SS-TuM-10 Using Photon-Stimulated Desorption to Probe the Structure and Reaction Dynamics of Molecules Adsorbed on $TiO_2(110)$***, **Greg Kimmel**,* Pacific Northwest National Laboratory **INVITED**

TiO_2 is a widely used photocatalyst. Its ability to oxidize organic contaminants makes it useful, for example, in air and water purification systems and as a thin-film coating for self-cleaning surfaces. As a result of titanium dioxide's practical applications and its potential use in photocatalytic water spitting, it has been the subject of a tremendous amount of research. We have investigated the photon-stimulated reactions of small molecules, such as O_2, CO, and acetone, on rutile $TiO_2(110)$. Experiments on clean, well-characterized single crystal surfaces, including azimuth- and angle-resolved measurements of photo-desorption products, provide key insights into the photochemical reactions of interest. This talk will highlight examples of this approach, including the photochemistry of chemisorbed O_2, the photo-oxidation of CO, and the photon-stimulated reactions of acetone. For the photo-oxidation of CO, the results show that a bridging O-O-C-O intermediate ejects CO_2 perpendicular to the bridging oxygen rows, which is consistent with density functional theory calculations. However, in contrast to earlier suggestions, the reaction kinetics show that the oxidation is a multi-step process. For acetone, the azimuth-resolved measurements of the methyl fragments revealed a second reaction channel that probably involves an enolate intermediate on the surface.

11:40am **HC+AS+SS-TuM-12 Comparison of Pt, Rh and Ir Single Atoms on a Fe_2O_3 Model Support***, **Gareth Parkinson**, A. Rafsanjani Abbasi, L. Puntscher, F. Kraushofer, P. Sombut, C. Wang,* TU Wien, Austria*; M. Meier,* University of Vienna, Austria*; M. Eder, J. Pavelec, G. Franceschi, M. Riva, M. Schmid, U. Diebold,* TU Wien, Austria*; C. Franchini,* University of Vienna, Austria

Understanding how the local environment of a “single-atom” catalyst affects stability and reactivity remains a significant challenge. Fe_2O_3 is the most common iron-oxide support material utilized for SAC, but little is known about how metal adatoms bind at its surfaces. In this talk, I will compare and contrast the behavior of Pt, Rh,[1,2] and Ir atoms on the flat, well-ordered (1×1) termination of Fe_2O_3(1-102).[3,4] Using a combination of scanning probe microscopy and spectroscopic data, as well as theoretical calculations, I will demonstrate significant differences between the adsorption site and thermal stability of the metals, as well as differences in their interaction with water and carbon monoxide.

[1] F. Kraushofer *et al.*, Single Atom Catalysts: Surface Reduction State Determines Stabilization and Incorporation of Rh on α-Fe_2O_3(1-102) (Adv. Mater. Interfaces 8/2021). *Advanced Materials Interfaces***8**, 2170045 (2021).

[2] F. Kraushofer *et al.*, Single Rh Adatoms Stabilized on α-$Fe_2O_3(1\bar{1}02)$ by Coadsorbed Water. *ACS Energy Letters***7**, 375-380 (2022).

[3] F. Kraushofer *et al.*, Atomic-Scale Structure of the Hematite α-Fe_2O_3(1-102) “R-Cut” Surface. *J. Phys. Chem. C***122**, 1657-1669 (2018).

[4] G. Franceschi *et al.*, A Model System for Photocatalysis: Ti-Doped α-Fe_2O_3(1-102) Single-Crystalline Films. *Chem. Mater.***32**, 3753-3764 (2020).

12:00pm **HC+AS+SS-TuM-13 HC Graduate Student Finalist Talk: Preparation and Characterization of Model Homotopic Catalysts: Rh Adatoms, Nanoparticles, and Mixed Oxide Surfaces on Fe_3O_4(001)***, **Marcus Sharp**,* PNNL/WSU*; C. Lee, M. Mahapatra, S. Smith, B. Kay, Z. Dohnálek,* PNNL

Single atom catalysts have emerged as a new catalyst frontier due to the need for improved catalyst activity and selectivity. Yet key fundamental challenges exist regarding understanding of how their activity and stability depend on their coordination environment. Surface science studies have the tools necessary to investigate such monodispersed single atom catalysts and their chemistry under well-controlled reaction conditions. Here, we have studied the behavior of Rh on the Fe_3O_4(001) single crystal surface using X-ray photoelectron spectroscopy (XPS), temperature programed desorption (TPD), and scanning tunneling microscopy (STM). We employ the Fe_3O_4(001) reconstructed surface that has been shown to stabilize single 2-fold coordinated metal adatoms to elevated temperatures. By varying the Rh deposition and annealing temperature, we have identified a series of model catalysts possessing unique Rh sites. These catalysts include Rh adatoms, mixed surface layers with octahedrally-coordinated Rh, small Rh clusters, and large Rh nanoparticles on both mixed and pure Fe_3O_4 surfaces. STM and XPS are used to characterize the Rh coverage, species, binding, and particle size distribution. Subsequently, CO and CO_2 adsorption is employed to characterize the chemical and redox properties of these sites. CO binds strongly with Rh adatoms, clusters, and nanoparticles desorbing at higher temperatures but interacts weakly with the Rh-octahedral species. In contrast, CO_2 interacts most weakly with Rh adatoms and nanoparticles, while interactions between Rh-octahedral and Fe-octahedral are indistinguishable. Further, CO_2 is used to distinguish between metallic Rh sites and Fe_3O_4(001) sites, which shows good agreement with our STM results. These model systems allow us to directly investigate reaction mechanisms on different types of catalytic sites furthering our understanding of how to selectively tune catalyst sites for desired reaction pathways. Future studies are directed toward understanding the energetics and reaction pathways of the hydrogenation of unsaturated hydrocarbons and carbonyl functional groups.

Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+2D+AS+BI+HC+LS+NS-TuA

In Situ Microscopy, Spectroscopy and Processing at Liquid-Solid-Gas Interfaces

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

2:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-1 Understanding Charge Carrier Variations on the Nanoscale Using Microwave Near-Field Microscopy***, **T. Mitch Wallis**, S. Berweger, P. Kabos,* National Institute of Standards and Technology **INVITED**

Understanding the spatial distributions of charge carriers and their polarity in nanoscale semiconductors and their devices remains a long-standing challenge. Scanning probe-based microwave impedance microscopy (MIM, also called scanning microwave microscopy, SMM) can directly probe charge-carriers on the nanoscale via the high-frequency capacitive interaction between the sharp tip and sample of interest.

Here we will first provide an overview of MIM, including applications to model systems. We will then focus on studies of active devices of semiconducting materials, including GaN nanowires and 2D crystals of elemental tellurium. We will conclude with an overview of recent efforts on photoconductivity mapping in 2D materials and hybrid organic-inorganic lead-halide perovskite thin films. In particular, for the latter we leverage the high bandwidth inherent in the microwave signal to obtain temporal resolution as high as 5 ns.

3:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-3 Oxidation/Reduction of Cu Nanoparticles at a Single-Layer Graphene/Electrolyte Interface Monitored by Scanning Kelvin Probe Microscopy***, **Sidney Cohen**, S. Khatun, M. Andres, I. Pinkas, I. Kaplan-ashiri, O. Brontvein,* Weizmann Institute of Science, Israel*; I. Rosenhek-Goldian,* weizmann Institute of Science, Israel*; R. Weatherup,* Oxford University, UK*; B. Eren,* Weizmann Institute of Science, Israel

The need to probe chemical and physical processes occurring in at liquid/solid interfaces at small scales is being addressed by several cutting-edge techniques. Scanning probe microscopy (SPM) is now a well-established tool for simultaneous morphological, electrical, and mechanical characterization at the nanoscale. Scanning Kelvin Probe microscopy (SKPM) is an SPM method which can measure the work function at nm distance scales. This technique is not conveniently applied within a solution environment. In this work, micro-electrochemical cells were capped by a single layer graphene upper membrane which is transparent to the electrostatic field, enabling high resolution surface measurements of electrical processes occurring at the interfacial liquid region below the membrane. This talk will present this set-up, and show how it can be used to examine stability, and surface interactions in the oxidation/reduction processes of copper nanoparticles (NPs) attached to the graphene under operating (operando) conditions. Complementary techniques including cyclic voltammetry, and ex-situ electron microscopy and x-ray photoelectron spectroscopy gave a complete description of the processes. As an established catalyst for CO_2 reduction, the behavior of Cu in electrochemical conditions is of great interest in both science and technology. The measurements described here provided a nm-scale view of differences in Cu NP oxidation in ambient air and electrochemical conditions, detecting both a galvanic corrosion in air, and reversible reduction of the NPs at cathodic potentials in alkaline solution. Detachment of the NPs after long measurements of redox cycling is documented and rationalized.

3:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-4 Investigation Tritium and Lithium transport along the Tritium-Producing Burnable Absorber Rod***, **Jiyoung Son**,* Pacific Northwest National Lab*; J. Gao,* PNNL*; G. Sevigny, S. Tripathi, B. Matthews,* Pacific Northwest National Lab*; X. Yu,* Oak Ridge National Laboratory

The compositional and microstructural changes in functional materials are critical for nuclear materials in fusion and fission applications. We investigated tritium (^{3}H) and lithium isotope (^{6}Li, ^{7}Li) transport within a neutron-irradiated target rod, aka, Tritium-Producing Burnable Absorber Rod (TPBAR), used in a light water reactor. TPBARs employ the iron aluminide-coated austenitic stainless-steel cladding and associated cruciform as key components. We used multimodal imaging tools and studied the specimens from irradiated TPBAR components. Specifically, a scanning electron microscope with focused ion beam (SEM-FIB) was used to prepare lift-out samples of the irradiated coating and cruciform samples for follow-up microanalysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was utilized to detect light isotopes in relation to tritium and lithium diffusion and transport. The observed distributions in the irradiated cladding specimens suggest light isotope mobility between internal target components as a result of neutron irradiation. We compared irradiated claddings of two different configurations in SIMS, and the chemical mapping and depth profiles of aluminide coatings show distinct light isotopic distributions. The cruciform specimens extracted from corresponding locations to the claddings also give interesting results. Overall, advanced correlative imaging results confirm tritium diffusion and lithium transport during the tritium production process. Such results give new insights into the fundamental transport mechanism within the target during irradiation and under non-equilibrium, extreme conditions.

4:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-7 Development of a Workflow for Multiscale Elemental Analysis with X-ray Fluorescence Microscopy and Tomography***, **Si Chen**,* Argonne National Lab*; Y. Luo,* Argonne National Laboratory*; T. Paunesku,* Northwestern University*; O. Antipova, Y. Liu, N. Zaluzec, Z. Di,* Argonne National Laboratory*; G. Woloschak,* Northwestern University **INVITED**

Scanning X-ray fluorescence (XRF) microscopy and tomography provides powerful capabilities to assess the elemental distribution in a three-dimensional (3D) space and differentiate their inter- and intra-cellular interactions in complex biological cells and tissues. Like other microscopy techniques, there is often a tradeoff between spatial resolution and field-of-view that each XRF instrument can provide. For example, XRF nanoprobes are specialized for analysis with <50 nm resolution, but the region can be analyzed within a reasonable time frame is limited to only a few tens of microns. Therefore, the capability to combine the use of multiple instruments becomes important for hierarchical analysis.

In this presentation, we will discuss the Bionanoprobe (BNP) instrument and applications. The BNP is an XRF nanoprobe located at the Advanced Photon Source of Argonne National Laboratory. It is dedicated to the studies of biological tissues and cells with a subcellular spatial resolution. In conjunction with a microscale-resolution XRF instrument, we have demonstrated a workflow to perform multiscale elemental mapping and tomography on HeLa cells treated with non-targeted nanoparticles. While nanoscale tomography revealed the nanoparticle distribution in individual cells, statistical information on cell-nanoparticle interaction was obtained with the microprobe from a large population of cells.

It is important to note the challenges in sample preparation for such multiscale analysis across platforms. Different instruments often require different specimen dimensions in order to achieve their optimal performance. To enable analysis on the same specimen, we have introduced an intermediate specimen manipulation step between micro- and nano-scale measurements utilizing focused ion beam (FIB). Local regions of interest identified with the microprobe were isolated with a FIB instrument and further analyzed at the BNP. Angular enlargement for tomography data collection enabled by the FIB operation significantly improved the tomography reconstruction quality.

5:00pm **CA+2D+AS+BI+HC+LS+NS-TuA-9 in Situ Molecular Imaging of Green Solvents for CO_2 Capture***, **Xiao-Ying Yu**,* Oak Ridge National Laboratory, USA

Switchable ionic liquids are emerging green solvents in for carbon dioxide (CO_2) capture, cleaner separation, and efficient biomass production.However, the liquid structure and composition of SWILs are not fully understood.Besides off-line analyses using NMR and IR, our knowledge of the sustainable green solvents is limited.We used in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study such solvents in this work.This is a unique in situ molecular imaging technique enabled by the invention of a vacuum compatible microfluidic reactor termed system for analysis at the liquid vacuum interface (SALVI).Green solvents of interest were synthesized and reported previously. They were introduced into the microfluidic channel for in situ analysis using liquid ToF-SIMS.Two model systems are illustrated in this talk.The first consists of 1, 8-diazabicycloundec-7-ene (DBU) and 1-hexanol with different CO_2 loadings.The second has koechanol with various CO_2 loadings.Koechanol acts as both acid and base in the latter.Our results show two coexisting liquid phases in these green solvents.This phenomenon was only hypothesized in previous theory prediction.We provide the first physical evidence of the complex liquid – liquid (l – l) interface using three-dimensional chemical mapping with submicrometer resolution.In addition, more complex stoichiometry is discovered due to CO_2 uptake.More importantly, we have provided the first chemical spatial visualization elucidating the evolving l – l interface.The more detailed molecular level understanding of the liquid structure and composition are instrumental to build the foundation for predicative material synthesis, CO_2 capture, and other versatile applications.

5:20pm **CA+2D+AS+BI+HC+LS+NS-TuA-10 Depth Dependence of Salt Ions at the Liquid/Vapor Interface Studied by Ambient Pressure X-Ray Photoelectron Spectroscopy**, *A. Siebert, K. Goodman,* ***Monika Blum,*** LBNL

Liquid/vapor interfaces play an important role in chemical, biological, technological, and environmental processes. Perhaps one of the most important interfaces for the environment is the interface between atmospheric aqueous aerosols and the surrounding air, which affects reactions like the scattering and absorption of sunlight as well as the probability of aerosols to serve as cloud condensation nuclei. [1,2] However, the experimental investigation of this active region is complicated by the necessary pressures far away from the ultra-high-vacuum (UHV) region, which is usually required in most surface science studies.[3]

In the recent past, ambient pressure X-ray photoelectron spectroscopy (APXPS) has proven to be a very powerful tool to study the chemical and electronic structure of liquids, solutions, and their interfaces with different media, not requiring the UHV conditions of standard XPS measurements. In this contribution we will utilize a colliding micro flat jet system with synchrotron-based APXPS to gain full insight into the depth dependency of different aqueous salt solutions, e.g. $CaCl_2$,at low salt concentrations. We will present a comparison of bulk ion concentrations in aqueous salt solutions and the surface ion concentration obtained from the ratio between the probed core level area and the peak area of the liquid water phase. This allows us to model the depth profile of salt ions in aqueous solutions and to correlate the data with existing theoretical models.

[1] Havala O. T. Pye et al., Atmos. Chem. Phys., 20, 4809–4888, 2020. [2] Barbara J. Finlayson-Pitts, Phys. Chem. Chem. Phys., 2009, 11, 7760–7779.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-TuA

Bridging Gaps I: Structural and Dynamic Effects in Catalysis

Moderator: Dan Killelea, Loyola University Chicago

2:20pm **HC+AS+SS-TuA-1 Fundamental Studies of C1 Catalysis on Metal-oxide and Metal-Carbide Interfaces**, ***Jose Rodriguez,*** Brookhaven National Laboratory **INVITED**

The transformation of CO_2 and CH_4 into alcohols or other hydrocarbon compounds is challenging because of the difficulties associated with the chemical activation of this highly stable molecules by heterogeneous catalysts. Pure metals and bimetallic systems used for this task have usually trouble binding CO_2 or CH_4 and, thus, low catalytic activity. Here, we will discuss a series of in-situ studies investigating different mechanisms or approaches for C-O and C-H bond activation. They illustrate the advantages of metal-oxide and metal-carbide interfaces when aiming at the conversion of CO_2 or CH_4 into methanol. CeOx/Cu(111), Cu/CeOx/TiO_2(110) and Cu/TiC(001) exhibit an activity for the $CO_2 \rightarrow CH_3OH$ conversion that is 2-3 orders of magnitude higher than that of a benchmark Cu(111) catalyst. In the Cu-ceria and Cu-TiC interfaces, the combination of metal and oxide (or carbide) centers affords complementary chemical properties that lead to special reaction pathways for methanol synthesis. Metal-oxide and metal-carbide interfaces also can be tune for the activation and conversion of CH_4.

3:00pm **HC+AS+SS-TuA-3 Atomic Scale Studies of Chromium Species on Iron Oxide Surfaces**, ***Moritz Eder,*** TU Wien, Austria*; P. Sombut,* University of Vienna, Austria*; C. Wang, L. Puntscher, A. Rafsanjani-Abbasi, M. Meier, J. Pavelec, G. Franceschi, M. Riva,* TU Wien, Austria*; C. Franchini,* University of Vienna, Austria*; M. Schmid, U. Diebold, G. Parkinson,* TU Wien, Austria

Chromium (Cr) ferrite catalysts are industrially employed for the water gas shift reaction in order to provide large amounts of molecular hydrogen.[1] However, the European REACH legislation demands that hexavalent Cr be banned from all catalysts used in industrial processes due to its toxicity. Consequently, alternative metals are sought to fulfill the role of Cr species in the corresponding compounds.[2] It is therefore necessary to obtain a fundamental understanding and characterization of Cr on iron oxides.

In this talk, we present the investigation of Cr species on Fe_3O_4(001) by means of STM and XPS at room temperature. We show the behavior during exposure to water gas shift reactants (i.e., CO and H_2O) and upon high temperature treatment. The latter is of utmost importance since the water gas shift reaction is conducted at temperatures up to 500°C.[1] The results are compared to the behavior of other transition metals and discussed with respect to implications for applied catalysis.[3]

[1] Häussinger, Lohmüller, Watson, *Hydrogen, 2. Production*. In: Ullmann's Encyclopedia of Industrial Chemistry, 2011

[2] Glassner, *Int. Surf. Technol.***14**, p. 36, (2021)

[3] Bliem, Pavelec, Gamba, McDermott, Wang, Gerhold, Wagner, Osiecki, Schulte, Schmid, Blaha, Diebold, Parkinson, *Phys. Rev. B* **92**, p. 075440 (2015)

3:20pm **HC+AS+SS-TuA-4 Investigation of CO Oxidation on Oxygenated Rh(111) Surfaces with RAIRS**, ***Elizabeth Jamka,*** *D. Killelea,* Loyola University Chicago

Surface IR spectroscopy is a quantitative technique that also provides information about the binding sites and chemical environments of the adsorbed CO molecules. In this research we are able to interface a FTIR to the ultra-high vacuum (UHV) chamber as a non-destructive and highly sensitive surface analysis technique. Because IR measurements can be performed in UHV conditions, interference from atmospheric species are avoided, while enabling investigation of catalytic systems, like carbon monoxide (CO) to carbon dioxide (CO_2) on Rh(111). To determine the reactivity of the various oxide phases, the oxidation reaction of CO to CO_2 on oxidized Rhodium (Rh) will be utilized as a probe reaction. Studying CO oxidation on different Rh surfaces will provide atomic level information regarding oxidation reactions, progressing the understanding of various surface phases relevant to many Rh catalyzed processes. This research focuses on CO sticked to clean Rh(111), (2x1)-O/Rh(111), and (2x1)-O + RhO_2/Rh(111). Via FTIR, these and other reaction sites of CO oxidation will be investigated to determine reaction pathways or mechanisms.

4:20pm **HC+AS+SS-TuA-7 Molecular Beam Surface Reaction Experiments with Chiral Molecules**, ***Tim Schäfer,*** Georg August University, Goettingen, Germany **INVITED**

Chirality is a feature of asymmetry describing the geometrical property of objects that cannot be mapped onto their mirror images like our hands as classic example. In chemistry, one observes chirality on the molecular level: two mirror images of chiral molecules (enantiomers) have only little difference in the structure, but this might cause a vast change in the biological activity.

Unfortunately, a fundamental understanding of chemical processes in chiral environments is challenging, as enantiosensitive detection methods must introduce chirality to distinguish enantiomers. Until recently, enantiospecific assignment of chiral gas phase molecules at low concentrations was not even possible. In the last decade, new enantiosensitive detection techniques have been invented based on photoionization of molecules (Photoelectron Circular Dichroism, PECD). Our group contributed to these advances by developing a unique technique that combines PECD with surface science. This approach allows the investigation of dynamics and kinetics of surface reactions of chiral molecules at the gas surface interface.

We use this technique for studies on heterogeneously catalyzed chiral surface reactions like the partial oxidation of olefins to epoxides on metal surfaces. For this, we combine PECD measurements with velocity resolved kinetics experiments, providing enantiosensitive information about reaction mechanisms at surfaces.

5:00pm **HC+AS+SS-TuA-9 A Local View on the Influence of Solvent and Product on the Reactivity of Surface-Catalyzed Reactions**, ***Karina Morgenstern,*** Ruhr Universität Bochum, Germany **INVITED**

Though largely influencing the efficiency of a reaction, the molecular-scale details of the local environment of the reactants are experimentally inaccessible hindering an in-depth understanding of a catalyst's reactivity, a prerequisite to maximizing its efficiency. We introduce a method to follow individual molecules and their largely changing environment during laser-induced reactions. The method is illustrated with a single-molecule resolution on two examples, the dissociation of halogenated benzene molecules adsorbed on ice [1] and of CO_2 on two catalytically relevant surfaces, Ag(100) and Cu(111)[2]. Dissociation of halobenzene is triggered by delocalized excess electrons. The adsorption on ice sufficiently lowers the energy barrier for the transfer between themolecular orbitals to facilitate dissociation of bromo- and chloro- but not of fluorobenzene at cryogenic temperatures.For the CO_2dissociation, we reveal how the reactant's surroundings evolve with progressing laser illumination and with it their propensity for dissociation. Our results shed light on the influence of solvent and products on reaction yields on the nanoscale.

[1]P. Auburger, I. Kemeny, C. Bertram, M. Lingges, M. Bockstedte, U. Bovensiepen, K. Morgenstern, Phys. Rev. Lett. 121, 206001 (2018)

[2] M. Vyshnepolsky, Z.-B. Ding, P. Srivastava, P. Tesarik, H. Mazhar, M. Maestri, K. Morgenstern, Angew. Chem. Int. Ed. 60, 18217-18222 (2021)

5:40pm **HC+AS+SS-TuA-11 Enhanced Catalytic Selectivity Due to Topographically Reduced Work Function of Carbon Nanospikes***, Arthur P. Baddorf,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; A. Rondinone,* Center for Integrated Nanotechnologies, Los Alamos National Laboratory*; D. Hensley,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Carbon nanospikes show excellent Faradaic efficiency and selectivity for electrochemical conversion of technologically important reactions, including CO_2 to ethanol in the presence of Cu [1] and N_2 to ammonia in the presence of Li [2]. Rates are higher than for other aqueous electrochemical approaches, including other low-dimensional carbon nanomaterials such as nanotubes, fibers, and foams, and much greater than for flat carbon surfaces. The essential attribute appears to be the sharp spike topography at which electric fields are enhanced. Transmission electron microscopy images reveal that films consist of a high density of nanospikes each 50-80 nm in height and terminated with a sharp tip of radius ~1 nm, i.e. a very high curvature.

We have explored the electric fields at the nanospikes by measurements of the absolute work function in comparison that of other carbon geometries using ultraviolet photoemission spectroscopy (UPS). As samples were characterized after transfer through air, surface cleanliness was monitored with x-ray photoelectron spectroscopy (XPS). Annealing as-grown samples above 275 °C was required to produce a clean surface which has a 4.13 eV work function, a half volt lower than that of flat graphite. This reduction supports the idea that a strong electric field is generated by the nanospike topography which contributes to the electrochemical activity.

Contamination of the spiked surface raises the work function above that of the clean nanospikes. Work function values following exposure increased to 4.19 eV for hydrocarbons, 4.30 for air, 4.42 for water, and 4.48 for oxygen. Blunting the spikes, by exposure to an oxygen plasma, argon sputtering, or annealing to 800 °C results in a work function close to that of flat graphite, 4.62 eV. An unusual double onset in the UPS secondary electron intensity is observed after absorbing hydrocarbons on clean nanospikes. This double onset has not been reported on metal surfaces and appears to be unique to carbon substrates. The energy difference between the two onsets, about 0.4 eV is close to that of a typical C-H stretch in hydrocarbons suggesting the lower energy onset may originate in inelastic scattering of photoelectrons.

* This work was supported by Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

[1] Y. Song, et al., Chemistry Select 1 (19), 6055 (2016).

[2] Y. Song, et al., Sci. Adv. 4(4)(2018).

6:00pm **HC+AS+SS-TuA-12 HC Graduate Student Finalist Talk: Enhanced Descriptor Identification and Mechanic Understanding for Catalytic Activity using Data-Driven Framework: A Case Study of CO Hydrogenation over Cu-Based Single Atom Alloys***, Wenjie Liao,* Stony Brook University/Brookhaven National Laboratory*; P. Liu,* Brookhaven National Laboratory and State University of New York at Stony Brook

Accurate identification of descriptors for catalytic activities has long been essential to the in-depth mechanic study of catalysis and recently to set the basis for catalyst screening. However, commonly used derivative-based local sensitivity analysis methods suffer from low accuracy in predictability. This study reports an enhanced approach to accurately identifying the descriptors from a kinetic dataset using the machine learning (ML) surrogate model. The CO hydrogenation to methanol over Cu-based single atom alloys was taken as a case study. Our model captures not only the contribution from individual elementary steps (i.e., first-order descriptors), but also the interaction between relevant steps within a reaction network (i.e., second-order descriptors), which was found to be essential for accuracy. As a result, six effective descriptors are identified, which are accurate enough to ensure the trained gradient boosted regression (GBR) model for well prediction of the methanol turn-over-frequency (TOF) over metal (M)-doped Cu(111) model surfaces (M = Au, Cu, Pd, Pt, Ni). More importantly, going beyond the purely mathematic ML model, the catalytic role of each identified descriptor can be revealed by using the model-agnostic interpretation tools, which enhances the mechanic insight into the promoting effect of alloying. The trained GBR model outperforms the conventional derivative-based methods in terms of both predictability and mechanic understanding.

The proposed data-driven framework allows one to identify key descriptors beyond rate-limiting steps while clearly depicting how each identified key descriptor would affect the catalytic activity when more than one activation energies were tuned. This approach can be applied to other reactions and catalysts, which opens alternative possibilities toward accurate descriptor-based rational catalyst optimization

Applied Surface Science Division
Room 320 - Session AS+BI+CA+HC+LS+PS+SE+SS-WeM
Analysis of Surfaces and Interfaces Related to Energy and the Environment

Moderators: Kateryna Artyushkova, Physical Electronics, **Tony Ohlhausen**, Sandia National Laboratory

8:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-1 Adhesion Properties of Industrial Steel Samples***, **Lukas Kalchgruber**, M. Hahn, L. Mears, M. Valtiner,* TU Wien, Austria

Solving industrial questions is of utmost importance to improve material properties, developing industrial applications and understanding fundamental processes. One of these questions is how different pre-treatments alter the adhesion process between steel and polymers.

To study the effect of the pre-treatment on the subsequent adhesion process, steel was treated either thermally or via plasma.

To characterize adhesion, the surface force apparatus (= SFA) was utilized in reflection mode. In the SFA experiment, the steel is brought into contact with another surface which is prepared on a fused silica optical disc. Before the optical discs can be used in SFA, a semitransparent, reflective layer needs to be deposited on the curved surface. Additionally, they were spin coated with few µm thin, homogeneous, smooth layers of SEBS polymer. Afterwards, a suitable particle free contact was established between the polymer and the steel sample in the SFA, which generated the following data types:

1. Newton rings à Provide information about the contact area
2. Force data à Adhesive pressure (referenced to contact area)
3. Fringes of chromatic order (= FECO) à Time-Distance-Curves

The main selling points of this technique are as follows: firstly, the model system is very close to the actual problem, as the steel sample in question can be used directly. Secondly, direct information about the adhesive pressure can be obtained. Thirdly, considerably more information about the adhesive behavior of the system is available beyond just one number.

The SFA results achieved are promising. We have a method that allows us to quantify the adhesive pressure in a model system and differentiate between differently treated steel samples. We have further put our adhesion results into context with the support of XPS characterization of the surface. Thermally treated samples have a hydroxide/oxide ratio of roughly 50/50 while samples treated with plasma show a ratio of 90/10. The hydroxide to oxide ratio correlates with the adhesion measured by SFA, which emphasizes the role of hydroxide in preventing adhesion.

8:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-2 An Electrochemically Polymerized Protective Layer for Magnesium Metal Anode***, Y. Wang,* University of Maryland College Park*; **Alexander Kozen,*** University of Maryland

Rechargeable magnesium (Mg) batteries are promising beyond Li-ion technologies due to their high volumetric capacity (3832 mAh cm^{-3}) and high natural abundance. Nonetheless, Mg metal anode is incompatible with most conventional electrolytes which leads to the formation of an ionically passivating layer. Mg also suffers from growth of dendrites similar to Li, which causes failure of the cells. In this study, we electrochemically polymerized 1,3-dioxolane (DOL) to form a thin Mg^{2+}-conducting elastomeric artificial solid electrolyte interphase (ASEI) layer by electrochemically pretreating Mg metal anodes. We found that this protective ASEI layer enables excellent cyclability of Mg-Mg symmetric cells at high current density (0.5 $mAcm^{-2}$) over 400 hours at a stable low overpotential (0.50 V vs. Mg^{2+}/Mg) without cell short-circuiting, while untreated pristine Mg symmetric cells quickly failed. The formation of this ASEI also significantly lowered the impedance of the cells, which proved its capability of conducting Mg^{2+} ions. Comprehensive surface chemistry analysis was done by X-ray photoelectron spectroscopy (XPS) which showed that an ASEI mainly consists of poly-DOL was formed, along with various Mg salts which are instrumental to the conductance of Mg^{2+} ions. More importantly, poly-DOL component in the elastomer was well preserved post-cycling, which contributed to the long-term cyclability and low voltage hysteresis of pretreated Mg-Mg cells, as compared to the pristine ones. Focused ion beam (FIB) – scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) mapping showed that a generally uniform layer was formed on the surface and this ASEI is roughly 200 µm thick and was able to suppress the growth of Mg dendrites after cycling for 400 hours at 0.03 mA cm^{-2} current density, as compared to the rampant sphere-shaped dendrites on the surface of pristine Mg anodes after cycling. This is the first ever report on the successful formation of poly-DOL ASEI on Mg metal anodes as a protective layer and by electrochemical polymerization method that effectively enhanced the electrochemical cycling performance of the Mg metal anodes.

8:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-3 Analysis of Surfaces and Interfaces in Polymer Electrolyte Membrane Fuel Cell and Electrolyzer Devices***, **Svitlana Pylypenko**,* Colorado School of Mines **INVITED**

Implementing a hydrogen-based infrastructure depends on developing electrochemical energy conversion devices such as fuel cells and electrolyzers. Polymer electrolyte membrane fuel cells (PEMFCs) have been the focus of research for lightweight renewable transportation applications such as motor vehicles for years, but they also offer the potential to fuel stationary applications, including residential power, due to their potential to produce industrial amounts of energy via a renewable route. Polymer electrolyte membrane water electrolysis (PEMWE) is a promising strategy to produce and store renewable energy in the form of hydrogen for subsequent use in either manufacturing processes, or to run a fuel cell, which can generate electricity on demand.

Great improvements have been made in the development of catalysts and electrodes for PEM systems, improving their activity and stability while reducing the amount of precious metals used. The properties of the electrodes used in these devices are influenced by multiple parameters: the chemical identity of the catalyst and the ionomer; the morphological properties of the catalyst (e.g. shape and surface area); ink formulations; and the various processing parameters used to prepare the electrode. Due to the breadth of possible variable combinations and the inherent complexity of electrode materials, it is unsurprising that PEM electrodes are both morphologically and chemically heterogeneous. Characterization of relevant surfaces and interfaces in these devices, therefore, represents a challenge that requires a multi-technique approach that evaluates all relevant scales and properties and brings a better understanding of the evolution of surfaces and interfaces under more realistic conditions. This talk will discuss the progress towards the comprehensive characterization of the most critical surfaces and interfaces in PEM devices using a combination of X-ray and electron spectroscopy and microscopy methods. Several challenges related to the characterization of catalyst-gas and catalyst-ionomer interactions in these systems will be covered along with results obtained with near-ambient pressure x-ray photoelectron spectroscopy (nAP-XPS). The development of characterization strategies to enable the exploration of a large processing parameter space will be presented, which can then be used to fabricate optimized electrodes with state-of-the-art catalysts as well as electrodes that integrate novel catalysts, all made with scalable routes. And finally, the development of novel approaches toward the characterization of other components of PEM devices such as porous transport layers will also be briefly discussed.

9:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-5 XPS Analysis of Battery Materials***, **Sarah Zaccarine**, B. Schmidt, K. Artyushkova,* Physical Electronics USA*; A. Baniya, Q. Qiao,* Syracuse University

Lithium-ion batteries (LIBs) have experienced success including rechargeability and long lifetimes but their limited energy density restricts applications moving forward. Lithium metal batteries (LMBs) offer similar benefits but with much higher achievable energy densities, making them a promising future battery technology. Both LIBs and LMBs are multi-layered, complex systems with many materials and interfaces that each play a critical role in performance and stability. Tuning the composition and morphology of these materials is necessary to create stable, high-performing devices, but the multi-component interfaces, interactions, and dynamic nature of these systems makes characterization challenging. In order to optimize materials properties and improve battery lifetimes, there is a pressing need for physicochemical characterization approaches with high spatial resolution, chemical and morphological analysis, and correlation of synergistic properties.

X-ray photoelectron spectroscopy (XPS) is commonly used to characterize the chemical composition of battery materials, and the depth resolution (~10nm) is ideal for analyzing thin layers and interfaces. However, modern XPS instruments have a variety of operating modes and analytical accessories that enable characterization across a variety of lateral and vertical size regimes. Small and large spot comparisons can track overall composition and local features and changes, with scanning microprobe analysis allowing for spatial resolution down to a few microns. X-ray induced secondary electron imaging (SXI), including high-resolution mosaic imaging over a wide sample area, can be used for easy identification of important features and morphological imaging of various battery component materials to complement chemical information. Chemical mapping can visualize distribution of individual elements or chemical species to understand how materials are distributed and change with testing. Additional options address stability concerns associated with Li materials, including a cooling stage to preserve battery chemistry during extended experiment times, where time-resolved profiles are used to compare chemical degradation under controlled temperatures, and incorporating Al Kα and Cr Kα X-rays for non-destructive XPS and hard X-ray photoelectron spectroscopy (HAXPES) analysis of surface (up to ~10nm, Al) and subsurface (up to ~30nm, Cr) composition. Combined, these powerful capabilities enable thorough characterization of battery materials properties for micro- and large-area spectroscopic analysis of surfaces and interfaces and how these properties change under various analytical and operating conditions.

9:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-6 Novel Battery Material Analysis with High-Resolution and High-Throughput XPS***, J. Counsell, S. Coultas,* Kratos Analytical Inc., UK*; C. Moffitt,* Kratos Analytical Inc.*; C. Blomfield,* Kratos Analytical Inc., UK*; **Adam Roberts**,* Kratos Analytical Limited, UK

Several material systems will be discussed to give an overview on how XPS can yield information regarding the distribution and chemical speciation of battery materials.

Na-ion batteries are considered to be environmentally favourable alternatives to Li-ion batteries, particularly in the extremely large-scale application of grid storage, given the abundance of Na. However, to date, the battery performance has not been competitive, and promising ternary materials have been plagued by poor stability in air and unsatisfactory long-term cycling. Herein, air/moisture stability is effectively and systematically investigated with XPS, paving the way for material stability to be modified through rational design. Chemical assignments were correlated with performance and oxidation degradation [1]

The significance of sensitivity and detection limit, comparisons of surface and bulk and an approach for pragmatic peak fitting of difficult elemental lines will be discussed along with considerations such as etch artefacts and degradation.

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11:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-10 Multimodal Analysis and Imaging of the Boehmite Layer on AA6061***, **Lyndi Strange**,* Pacific Northwest National Lab*; X. Yu,* Oak Ridge National Laboratory*; V. Shutthahandan, M. Song, Q. Miller, M. Bowden, J. Gao, Y. Zhang, J. Son, R. Shimskey, R. Prabhakaran,* Pacific Northwest National Lab*; V. Joshi,* Pacific Northwest National Laboratory

Low-enriched uranium (LEU) alloyed with 10% Mo (U-10Mo) is being considered as a promising alternative to oxide-based dispersion fuel with high-enriched uranium for use in research reactors. The configuration of this proposed LEU monolithic fuel plate consists of the U-10Mo plate-type fuel foil with a 25 µm Zr interlayer barrier clad with an aluminum alloy (AA6061). The clad AA6061 is coated with a boehmite layer to prevent corrosion. The boehmite layer has a high pH passivation range, which makes it resistant to oxidation and preferable to protect the Al cladding. Boehmite is usually formed on the AA6061 surface by autoclave processing. Various surface cleaning techniques have been employed such as polishing and etching to clean the surface of the AA6061 prior to boehmite formation. In this study, we examine how pre-treatment of AA6061 using polishing followed by both acid and alkaline etching affects the chemical composition of the boehmite layer using multimodal analysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS), x-ray photoelectron microscopy (XPS), transmission electron microscopy (TEM), and grazing incidence x-ray diffraction (GI-XRD) were used to understand the changes in the boehmite layer as a result pre-treatment. ToF-SIMS provides a surface sensitive technique to understand the surface composition and characteristics. Spectral similarities were verified using principal comment analysis (PCA). XPS is a complimentary technique that provides quantitative information about the oxidation states present on the surface. Both the SIMS and XPS results suggested oxidation at the surface, which was further investigated using TEM-SAED and GI-XRD. While the GI-XRD results suggested the dominant phase present on the coupon surface is boehmite, TEM-SAED found small amounts of α- and γ-Al_2O_3 present as a result of alkaline etching.

11:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-11 Study of $Cs_x(CH_3NH_3)_{1-x}PbBr_3$ Perovskite with XPS Imaging and Small Area Spectra***, **Tatyana Bendikov**,* Weizmann Institute of Science, Israel*; Y. Rakita,* Columbia University*; H. Kaslasi, G. Hodes, D. Cahen,* Weizmann Institute of Science, Israel

Interest in halide perovskite (HaPs) is motivated by the combination of superior optoelectronic properties and ease in synthesizing these materials with a surprisingly low density of electrically active defects.[1] HaPs possess high chemical sensitivity, especially those having an organic cation at their *A* position (*AMX_3*). Although a direct role of the *A* cation in this sensitivity is unclear, and the structural and optoelectronic backbone lie within the *M-X* bond, the type of the *A* cation was shown to impact the chemical stability and, usually indirectly, affect optoelectronic properties of HaPs.[2-3]

X-ray Photoelectron Spectroscopy (XPS), is a surface sensitive technique with a sensitivity that goes down to a single atomic layer, and can provide unique information that relates the elemental composition with the chemical and electronic states of the different elements in the material. Our study focuses on the XPS imaging in combination with selected small area XPS spectra and uses solution-grown, single crystals of mixed *A*-cation $Cs_xMA_{1-x}PbBr_3$($MA = CH_3NH_3^+$) HaPs as a candidate for investigating heterogeneity within the crystals. With XPS we followed the variations in chemical composition of these crystals. By observing the surface, we found significant changes in the N/Cs ratio, which increases towards the interior of the crystal. Similar variations in N/Cs, but also in Pb/(N+Cs) ratios were found when we studied cross-sections of cleaved crystals. This compositional heterogeneity within the HaPs crystal was not previously reported and was discovered and monitored due to exclusive capabilities of the XPS technique.

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11:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-12 Surface Characterization of Mineral Associated Organic Matters in Environmental Samples by Using X-Ray Photoelectron Spectroscopy (XPS)***, **Qian Zhao**, M. Engelhard, O. Qafoku, K. Hofmockel,* Pacific Northwest National Laboratory

Surface characterization is an important analytical approach to understanding the most dynamic interface of a material. The understanding of soil organic matter (SOM) persistence is critical to global carbon (C) cycling. Minerals play an important role in persisting SOM by associating with organic matters (OM) through different interactions. Yet mechanisms of the accumulation of OM in soil are still unclear. Chemical characterization of OM that is associated with minerals provides a mechanistic understanding of mineral-OM interactions. X-ray photoelectron spectroscopy (XPS) analysis allows us to probe the chemical states and speciation of OM on the surface of mineral grains or soil particles. This work used both synthetic mineral-OM complexes and natural soil samples to investigate the chemistry of organics that associate with minerals. In the synthetic system, we adsorbed four organic compounds on a calcite crystal. XPS analysis found the relative concentration of C was higher in OM adsorbed calcite than that in pristine calcite. Further, the deconvolution of C 1s spectra reveals that the calcite surface had a relatively lower abundance of carbonate but a higher abundance of alkanes in the OM adsorbed calcite than pristine calcite, indicating the adsorption of OM on the calcite surface. In the soil system, we incubated agricultural soils with ^{13}C-glucose for 12 months to trace the fate of microbial residues. Size and density fractionation was used to separate mineral-associated organic matter (MAOM) from whole soil. XPS analysis determined C chemistry of necromass on soil particle surfaces by scanning C 1s region of MAOM and non-MAOM fractions. We found that the MAOM fraction had a relatively higher abundance of carbonyl and carboxylic C functional groups and a relatively lower abundance of C-C/C=C group than non-MAOM fraction. It suggests that MAOM fraction is enriched in microbial-derived molecules (i.e., proteins) but has fewer plant detritus (i.e., carbohydrates or lignin) on mineral surfaces. XPS technique allows us to understand the surface chemistry of microbial necromass that is associated with minerals in soil. The chemical speciation information provides us with the potential bonding environment at the interface of minerals and OM.

Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+HC+LS+VT-WeM

Multiphase Interfacial Analysis and Imaging

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), **Slavomir Nemsak**, Advanced Light Source, Lawrence Berkeley National Laboratory

8:00am **CA+HC+LS+VT-WeM-1 Probing the Impact of Nanoscale Defect Sites in Perovskite Photovoltaic Films with Time-Resolved Photoemission Electron Microscopy*, Keshav Dani,*** 1919-1 Tancha, Kunigami-kun, Japan **INVITED**

Hybrid perovskite photovoltaic devices have rapidly emerged as promising contenders for next generation, low-cost solar cell technology. Yet, the presence of defect states critically impacts device operation, including device efficiency and potentially long-term stability. Understanding the nature of these defects, and their role in photocarrier trapping, requires techniques that are capable of probing ultrafast photocarrier dynamics at the nanoscale.

In this talk, I will discuss the development of time-resolved photoemission electron microscopy (TR PEEM) techniques in my lab [1, 2], applied to hybrid perovskite solar materials. Thereby, we directly visualize the presence of the performance limiting nanoscale defect clusters and elucidate the role of diffusion in the charge carrier trapping process [3]. By correlating PEEM measurements with other spatially resolved microscopies, we identify different types of defects that form, and study how passivation strategies may have a varied impact on them [4]. Finally, we show that these defect can act as seeds for degradation [5].

[1] M. K. L. Man, *et al.* Imaging the motion of electrons across semiconductor heterojunctions. *Nature Nanotech.***12**, 36 (2017).

[2] E. L. Wong, *et al.* Pulling apart photoexcited electrons by photoinducing an in-place surface electric field. *Science Advances***4**, eaat9722 (2018).

[3] T. A. S. Doherty*, A. J. Winchester*, et al.Performance-limiting trap clusters at grin junction in halide perovskites. *Nature***580**, 360 (2020). *equal authors

[4] S. Kosar, et al. Unraveling the varied nature and roles of defects in hybrid halide perovskites with time-resolved photoemission electron microscopy. *Energy Environ Sci*. 14, 6320 (2021)

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8:40am **CA+HC+LS+VT-WeM-3 Correlating Structure and Chemistry Using Ambient Pressure Photoemission and X-Ray Scattering*, Slavomir Nemsak,*** Lawrence Berkeley Laboratory Advanced Light Source **INVITED**

In the last two decades, Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) has established itself as a go-to technique to study heterogeneous and complex materials under reaction environments. Multimodal approaches, which correlate information from two or more complementary techniques, are currently one of the forefronts of the APXPS development [1]. In the past three years, the ALS contributed one such setup: a combined Ambient Pressure PhotoEmission and X-ray Scattering (APPEXS) instrument commissioned and operated at beamline 11.0.2 [2]. The combination of the two in-situ techniques allows correlating structural and chemical information. By using APPEXS, we observed dynamics of the exsolution process of catalyst metallic nanoparticles [3]. To expand the capabilities of APPEXS further, we introduced a new platform using arrays of patterned nanoparticles to study the evolution of catalytic systems under reaction conditions [4]. Future developments of the technique(s) will be also discussed.

References

[1] H. Kersell et al., Ambient Pressure Spectroscopy in Complex Chemical Environments, 333-358 (2021).

[2] H. Kersell et al., Rev. Sci. Instr. 92, 044102 (2021).

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[4] H. Kersell et al., Synchr. Rad. News, accepted (2022).

9:20am **CA+HC+LS+VT-WeM-5 Gating of the 2D Hole Transport in Diamond by Subsurface Charges***, E. Strelcov, **Andrei Kolmakov,*** NIST

The unique electronic, physical, and thermal properties of diamond make diamond-based FETs one of the most prospective devices for high-frequency power electronics. Transfer doping of hydrogenated diamond is a common process to form 2D conducting channels in diamond FET. The electron /hole transport of such a device is sensitively dependent on near-surface scatters including charged traps.

Here, using SEM (EBIC) and AFM Kelvin probe force (KPFM) microscopies we report on imaging of the hole transport in narrow conducting channels as a function of the density and depth of near-surface charges. We demonstrate the gating effect induced by trapped charges and discuss the methods to minimize these effects.

9:40am **CA+HC+LS+VT-WeM-6 Development of 0–D Argon Collisional Radiative Model conjoined with Optical Emission Spectroscopy between 1 mTorr to 760 Torr*, Tag Choi*,** *N. Abuyazid, D. Patel,* University of Illinois at Urbana-Champaign*; D. Jacobson,* LytEn. Inc*; S. Keniley, S. Dubowsky, D. Barlaz, D. Curreli, D. Ruzic,* University of Illinois at Urbana-Champaign

Optical emission spectroscopy (OES) is a non-invasive plasma diagnostic, which can be utilized with 0-dimensional argon collisional radiative model (Ar CRM) to understand dynamics of excited and charged argon species and determine plasma parameters in the system. This work aims to study rate coefficients of excited and charged argon species, calculate their densities over time and verify the theoretical results with experimental optical spectra in a wide range of pressure regimes. The model considers various types of collisions such as electron and atom excitation/ionization, photon emission, diffusion, penning ionization, and excimer formation. A merit function is used to obtain a better correlation between the theoretical and experimental densities of the various argon species. This allows the model to get a more accurate estimate of the electron temperature and the densities. Various plasma sources are used such as a low pressure inductively coupled plasma (ICP) source, dielectric barrier discharge (DBD), and microwave discharges, to produce different types of plasmas at pressure ranges of 10 – 50 mTorr and 1 – 760 Torr. The optical emission spectra and Langmuir probe measurements are collected for verifications on a low pressure ICP source and DBD discharge. For the verification of atmospheric microwave discharge, OES data is collected for temperature calculations from Specair and the model. Different plasma sources produce different electron temperatures and densities. The ICP source, DBD and microwave discharge have electron temperatures (T_e) of 2 – 5 eV, 1 – 3 eV, and 0.4 – 0.6 eV and electron density (n_e) of 1E16 to 1E18 m^3, 1E18 to 1E21 m^3, and 1E19 to 1E22 m^3 respectively. A methane and argon gas mixture are introduced to the microwave discharge to understand how plasma parameters differ from a pure argon environment.

11:00am **CA+HC+LS+VT-WeM-10 Atomic-Scale Modeling of Bismuth and Argon Clusters Sputtering of Water/Vacuum Interfaces*, Zbigniew Postawa*,** *M. Kański, C. Chang, S. Hrabar,* Jagiellonian University, Poland **INVITED**

Modeling of water/vacuum interfaces should consider the high vacuum pressure of water. First, there is continuous evaporation of the liquid into the vacuum chamber, which must be considered. This phenomenon poses a significant challenge for conventional experimental techniques. Yang *et al.* presented a way to reduce the impact of this phenomenon by using a microfluidic channel [1]. This approach uses an ion beam to drill a 2-3 µm window in the channel wall, exposing the liquid flowing below. Such an arrangement allows for maintaining a low base pressure ($\sim10^{-7}$ mbar) in the measuring chamber. This technique has already been used to study photochemical reactions, biofilms, and liquid-liquid interfaces by secondary ion mass spectrometry or secondary electron microscopy [2]. Recently, another approach minimizing the effect of high vacuum pressure of water that uses a graphene cell encapsulating a liquid was proposed in studies with transmission electron microscopy [3].

Recently, we have developed a new ReaxFF potential parameterization for modeling C/H/O systems designed directly for sputtering simulations [4]. This parametrization is up to 3 times faster than standard ReaxFF. New force-field allowed us to perform molecular dynamics computer simulations of water and graphene-covered water systems sputtered by bismuth and argon clusters. The mechanism of molecular emission from these two systems is investigated. The effect of the projectile size and the influence of the protecting graphene sheet on the emission process is discussed.

References

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Acknowledgments

The work has been supported by Polish National Science Center Grant 2019/33/B/ST4/01778 and the PLGrid Infrastructure.

11:40am **CA+HC+LS+VT-WeM-12 Finite-Elements Modeling of Solid-Electrolyte Interfaces in Through-Membranes Imaging and in-Liquid Scanning Probe Experiments*, Alexander Tselev,*** Department of Physics & CICECO-Aveiro Institute of Materials, University of Aveiro, Portugal **INVITED**

Studies of the physicochemical processes at the interfaces between solids and electrolytes interfaces require *operando* multi-parametric measurements with chemical and electric potential sensitivity, in-depth selectivity, as well as with a high lateral resolution. A number of experimental techniques were implemented for this purpose. In this talk, we will describe applications of finite-elements (FE) modeling to elucidate and interpret microscopic imaging and measurements with liquids ranging from non-polar ones to decimole electrolyte solutions. This includes probing through graphene membranes with the use of microscopy and spectroscopy tools based on high-energy beams—X-rays and electron beams, as well as low-energy probing with the use of scanning probe techniques. Scanning probe techniques can be implemented both with probes in liquids and with probes separated from the electrolytes by membranes. We will discuss liquid-solid interface probing by the Kelvin probe force microscopy (KPFM) through graphene membranes as well as by near-field microwave microscopy through dielectric membranes. Furthermore, models for piezoresponse force microscopy and KPFM with probes immersed in electrolytes will be presented. Support of this work by the project CICECO-Aveiro Institute of Materials, financed by national funds through the FCT/MEC (Portugal) and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement is acknowledged.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-WeM

Advances in Materials and Analysis in Heterogeneous Catalysis II

Moderators: Sanjaya Sennayake, Brookhaven National Laboratory, **Jason Weaver**, University of Florida

8:20am **HC+AS+SS-WeM-2 Development and Characterization of Highly Stable ALD Coated Catalysts for Dehydrogenation of Light Alkanes*, Jonathan Travis,*** *J. Burger, A. Dameron,* Forge Nano

Catalysts are critical materials for enabling many modern industrial chemical processes, such as the dehydrogenation of light alkanes to produce "on purpose" alkenes. Catalyst deactivation costs the chemical industry billions of dollars. One of the major mechanisms of deactivation is metal sintering during high temperature regeneration. Atomic Layer Deposition (ALD) overcoating has previously been demonstrated to stabilize catalyst materials against sintering and deactivation, as well as improve selectivity in certain cases. In this study the properties and performance of 0.1% Pt/Al_2O_3 catalysts are investigated as a function of surface modification via ALD Al_2O_3 coatings. The catalysts are characterized in Forge Nano's in-house catalyst characterization laboratory. Physical characterization is performed using various techniques including moisture analysis, BET Surface Area, Porosimetry, TGA, CO Chemisorption, ICP-MS, and Temperature Programmed Reduction, Desorption, and Oxidation. Performance is characterized using propane dehydrogenation under a variety of conditions. This talk will present the effects of Forge Nano's ALD Al_2O_3 coating on the properties and performance of the 0.1% Pt/Al_2O_3 catalysts.

8:40am **HC+AS+SS-WeM-3 Combining Theory with Ambient Pressure XPS to Reveal Chemistry at Interfaces Under *In Situ* and *Operando* Conditions*, Ethan Crumlin,*** Lawrence Berkeley National Laboratory **INVITED**

Interfaces play an essential role in nearly all aspects of life and are critical for electrochemistry. Electrochemical systems ranging from high-temperature solid oxide fuel cells (SOFC) to batteries to capacitors have a wide range of essential interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and converted. This talk will focus on using ambient pressure XPS (APXPS) to directly probe the solid/gas and solid/liquid electrochemical interface. APXPS is a photon-in/electron-out process that can provide both atomic concentration and chemical-specific information at pressures greater than 20 Torr. Using synchrotron X-rays at Lawrence Berkeley Nation Laboratory, the Advanced Light Source has several beamlines dedicated to APXPS endstations that are outfitted with various *in situ*/*operando* features such as heating to temperatures > 500 °C, pressures greater than 20 Torr to support solid/liquid experiments and electrical leads to support applying electrical potentials support the ability to collect XPS data of actual electrochemical devices while it's operating in near ambient pressures. This talk will share our efforts to combine theory and APXPS to understand the chemistry at solid/gas and solid/liquid interfaces under *in situ* and *operando* conditions. At the solid/gas interface, we will share our work to understand how carbon dioxide interacts with copper and silver surfaces using APXPS and theory to generate observables that we could experimentally verify. Separately I will introduce our strategy to introduce a chemical reaction network to generate spectra of water interacting with a silver surface that directly resembled our APXPS measurements. At the solid/liquid interface, the combination of theory and APXPS revealed how stable magnesium electrodes and stable diglyme electrolytes could be unstable when in contact with each other. In addition, it facilitated the prediction of the sensitivity for probing interfacial chemical species at a solid/liquid interface. To further advance these directions and synergy for combining theory and experiments, I will show our recent progress in creating an interfacial Digital Twin that we hope will rapidly accelerate our understanding of interfacial chemistry.

9:20am **HC+AS+SS-WeM-5 The Electrochemical Interface as a Reactive Environment to Resynthesize Electrode Surface Chemistry Using the Dissolution-Redeposition Dynamics*, Feng Lin,*** Virginia Tech **INVITED**

The solid-liquid electrochemical interface offers a two-dimensional environment for geometrically confined interfacial reactions to tailor electrode surface chemistry under operating conditions. Herein, we demonstrate that the dissolution and redeposition kinetics of transition metal cations, a ubiquitous phenomenon at the electrochemical interface, can be manipulated to regulate the chemical composition and crystal structure of the electrode surface as well as the overall electrochemical performance. Foreign cations, either added as electrolyte additives or dissolved from surface coatings, can rapidly participate in the electrode dissolution-redeposition process, and facilitate the establishment of the dissolution-redeposition equilibrium. We will present scientific case studies in electrocatalysis. Our work expands the control over the electrochemical reactions at the solid-liquid interface and provides new insights into interfacial studies in electrochemistry, and surface science.

11:00am **HC+AS+SS-WeM-10 Ambient Pressure Spectroscopy of Catalytic Porous Nanofilms**, *C. Eads,* MAX IV Laboratory, Sweden*; T. Hu, S. Tenney,* ***Ashley Head,*** Brookhaven National Laboratory **INVITED**

Porous materials offer an opportunity for catalysis in confined spaces. By spatially confining chemistry, reaction dynamics and selectivity can change in unknown ways. Two examples will be discussed, including Pt nanoparticles embedded in a thin film of the metal-organic framework UiO-66(NH_2) and a two-dimensional silicate on Pd(111). Ambient pressure X-ray photoelectron spectroscopy (APXPS) has been used to characterize the electronic structure of the Pt-embedded metal-organic framework. CO oxidation and CO_2 reduction have been followed with IR spectroscopy and mass spectrometry. In a second system, the space between a two-dimensional silicate and a Pd(111) surface promotes more CO oxidation than a bare Pd surface. IR spectroscopy shows that the silicate film changes the surface adsorbates, resulting in increased CO_2 formation, as confirmed with mass spectrometry. These results will help enable the rational design of materials to spatially confine reactions in a desired way.

11:40am **HC+AS+SS-WeM-12 Catalytic Oxidation of Methane on $IrO_2(110)$ Films*, Jovenal Jamir*,** *R. Martin,* University of Florida*; M. Kim,* Yeungnam University , Republic of Korea*; C. Lee, V. Mehar,* University of Florida*; A. Asthagiri,* The Ohio State University*; J. Weaver,* University of Florida

In recent years, $IrO_2(110)$ films have gained increasing interest for their ability to strongly adsorb light alkanes and cleave C-H bonds below room temperature. Our group has shown, via ultrahigh vacuum (UHV) temperature programmed reaction spectroscopy (TPRS) experiments, that initial methane activation occurs at temperatures as low as 100 K and leads to the desorption of CO, CO_2 and H_2O above 400 K. The large temperature range over which partially oxidized methane-derived species exist, along with the facile nature of C-H bond cleavage motivates further study of methane oxidation under catalytically relevant conditions. In this talk I will discuss recent kinetic studies performed in a batch reactor to investigate the catalytic oxidation of CH_4 on $IrO_2(110)$ films at gas pressures near 1 Torr as well as results of ambient pressure x-ray photoelectron spectroscopy (AP-XPS) measurements and molecular simulations. We find that $IrO_2(110)$ is highly active for the catalytic combustion of CH_4 at moderate temperatures (500-650 K), with comparable activities to PdO catalysts. Our results further show that catalytic CH_4 oxidation is mildly activated on $IrO_2(110)$ and that the catalytic rates depend slightly inversely on the O_2 partial pressure, suggesting that the dissociative chemisorption of O_2 is more efficient than CH_4 activation and acts to blocks CH_4 adsorption sites. AP-XPS measurements reveal that high coverages of OH groups and CH_yO_2 species form on $IrO_2(110)$ during CH_4 oxidation and that O-rich $IrO_2(110)$ surfaces are maintained even under highly CH_4-rich conditions (up to 95% CH_4), consistent with efficient O_2 adsorption and site competition with CH_4. Finally, I will discuss how we have combined our AP-XPS results with catalytic rate measurements to develop first principles, microkinetic models for methane oxidation over $IrO_2(110)$. Of particular significance is that earlier models did not consider surface CH_yO_2 species. Our AP-XPS results thus inspired efforts to identify additional reactions and determine the roles that various adsorbed species play during catalytic CH_4 oxidation on $IrO_2(110)$. Our findings highlight how operando surface spectroscopy can provide key guidance for understanding catalytic reaction mechanisms and developing accurate kinetic models.

12:00pm **HC+AS+SS-WeM-13 HC Graduate Student Finalist Talk: *Operando* Observation of Metal Encapsulation Causing Strong Metal-Support Interaction at the Pt-Co_3O_4 Interface*, Daeho Kim,*** Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; D. Park,* Korea Advanced Institute of Science and Technology, Republic of Korea*; H. Song,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; B. Jeong,* Korea Basic Science Institute (KBSI), Republic of Korea*; Y. Jung,* Korea Advanced Institute of Science and Technology, Republic of Korea*; J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Noble metal nanoparticles (NPs) supported on metal oxide (e.g., Co_3O_4, NiO, TiO_2, CeO_2, and Fe_2O_3) have been commonly utilized as a heterogeneous catalyst for improving catalytic performance and modifying the reaction pathway of various catalytic reactions, such as CO oxidation, CO_2 hydrogenation, and Fischer-Tropsch synthesis. The unique interaction at the interface of the metal NP and oxide, which is known as the strong metal-support interaction (SMSI), gives synergistic enhancement to the catalytic activity. Hence, a fundamental understanding of SMSI with bridging pressure and material gaps using operando surface characterization is necessary for developing high-performance heterogeneous catalysts.

Herein, we show the direct evidence of SMSI at the interface of Pt NP and Co_3O_4, utilizing operando surface analysis. The Pt-Co_3O_4 interfaces were prepared as powder catalysts using colloidal Pt NPs embedded on the mesoporous Co_3O_4. The two-dimensional model system is also constructed on Co_3O_4–coated Si wafer via a Langmuir-Blodgett trough to bridge the material gap. The surface of prepared Pt-Co_3O_4 is comprehensively characterized under dynamic conditions: a reducing environment (H_2 or CO) and a catalytic reaction environment (CO + O_2). Combining computational calculation and the operando surface characterizations using ambient pressure X-ray photoelectron spectroscopy, environmental transmission electron microscopy, and diffuse reflectance infrared Fourier-transform spectroscopy, we suggest that the interface between Pt NPs and the thin oxide overlayer is a key state of the SMSI enhancing the catalytic activity.

Surface Science Division

Room 319 - Session SS1+HC-WeM

Alloy Surface Reactivity

Moderator: Zdenek Dohnalek, Pacific Northwest National Laboratory

8:00am **SS1+HC-WeM-1 Development of a Predictive Model for Nb_3Sn Thin Film Growth: Elucidating the Substrate-Mediated Diffusion Pathways Guiding Alloy Formation in Accelerator Infrastructure*, Sarah Willson,*** University of Chicago*; R. Farber,* University of Kansas*; S. Sibener,* University of Chicago

Niobium is the current standard elemental material for superconducting radiofrequency (SRF) cavities, but the required operating temperatures (< 4 K) impose a significant monetary burden. To achieve improved accelerating gradients at increased operating temperatures, efforts are underway to vapor deposit Sn on preexisting Nb SRF cavities to form Nb_3Sn thin films. However, these Nb_3Sn coatings contain high surface defect densities and stoichiometric inhomogeneities; the accelerating performance of Nb_3Sn coated cavities is directly associated with the Nb_3Sn surface morphology. Current Nb_3Sn SRF cavities, therefore, are impractical for implementation in particle accelerator facilities. The implementation of Nb_3Sn SRF cavities necessitates a comprehensive and mechanistic understanding of how to form smooth and homogenous Nb_3Sn films.

To develop a predictive growth model for Nb_3Sn grown *via* Sn vapor deposition, we aim to understand the interplay between the underlying Nb oxide morphology, Sn coverage, and Nb substrate heating conditions on Sn wettability, intermediate surface phases, and Nb_3Sn grain growth dynamics. In this work, Nb-Sn intermetallic species are grown on a single crystal Nb(100) in an ultra-high vacuum chamber equipped with *in situ* surface characterization techniques including Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy/spectroscopy (STM/STS).

Sn adsorbate behavior on oxidized Nb was examined by depositing Sn with sub-monolayer precision at varying Nb sample temperatures (T_S). STM data of Sn deposited on a highly ordered NbO surface reconstruction reveal that the Nb T_S during deposition strongly dictates the competition between Sn incorporation and desorption during subsequent annealing. By tailoring Sn deposition parameters to suppress Sn desorption, AES and XPS data of annealed intermetallic adlayers provide supporting evidence of how Nb substrate oxidization and sample temperature impact Nb-Sn coordination. Ongoing experimental studies aim to demonstrate the impact of altering numerous vapor and substrate conditions on the growth mechanisms and alloying dynamics that ultimately enable optimal Nb_3Sn growth.

8:20am **SS1+HC-WeM-2 Surface Chemical Reactions in the Oxidation of NiCr and NiCrW Alloys*, Petra Reinke,*** *C. Volders,* University of Virginia, USA*; V. Avincola Angelici ,* University of Virginia*; I. Waluyo, A. Hunt,* Brookhaven National Laboratory*; L. Arnadottir,* University of Oregon

The oxidation of alloys including several reactive elements is controlled by complex reaction pathways where surface chemistry, reactant transport, alloy microstructure, oxide-alloy epitaxy and other factors compete. Our work focusses on the oxidation of Ni-based superalloys frequently used in technologies subjected to a wide range of environmental stressors from chemically aggressive solutions in sea water, batteries and fuel cells to radiation in nuclear waste containers. We address the socalled “third element effect” TEE where a relatively small addition of a specific element has an outsized impact on corrosion and oxidation processes. We specifically address the initial steps in the formation of the protective oxide layer starting with a pristine alloy surface. Significant gaps exist in the mechanistic understanding of the initial reaction steps of their oxidation. Near ambient pressure X-ray photoelectron spectroscopy, XPS and STM were used to study the oxidation with O_2*in operando* for a sequence of alloy compositions from Ni-5wt%Cr, Ni-15wt%Cr, Ni-30wt%Cr to Ni-15wt%Cr-6wt%W. The experiments were performed at 500 °C, $p(O_2)=10^{-6}$ mbar and reflect the initial 25 ms of oxidation at ambient conditions. The formation of Ni and Cr oxides competes under these conditions due to kinetic limitations imposed on the reaction of Cr, which is thermodynamically preferred.

The comparison of oxide evolution for four different alloys with variable Cr and W content quantifies the outsized impact of W as a minor alloying element. For the binary alloys an initial rapid increase in chromia driven by

Cr-surface enrichment is followed by NiO nucleation and growth, ultimately seeding a dual-layer structure. The addition of small amounts of W in Ni-15wt%Cr-6wt%W shifts the reaction pathways towards Cr oxidation revealing a high quality chromia layer which is desirable for its protective function. Density functional theory calculations inform that W atoms adjacent to Cr sites embedded in the Ni surface create even more favorable oxygen adsorption sites. In short, a larger Cr content in the surface enhances reaction with oxygen, but the addition of W "supercharges" the reactivity of Cr by funneling the oxygen atoms into Cr sites. The surface chemistry is identified as a decisive contribution to the TEE, and is accompanied by a enhanced grain boundary driven Cr transport in the alloy to sustain chromia growth.

8:40am **SS1+HC-WeM-3 High Throughput Methods for Comprehensive Study of Alloy Segregation and Structure Sensitivity**, ***Andrew Gellman**, C. Fernandez-Caban, Z. Guo, R. Burnley,* Carnegie Mellon University, USA **INVITED**

Comprehensive study of phenomena such as segregation in alloys or structure sensitivity in catalytic surface chemistry is hampered by the fact that the independent variables associated with these phenomena are continuous and multidimensional. In the case of alloy segregation, the relevant independent variable is alloy composition which is continuous and multidimensional in the case of ternary or higher order alloys. In the case of structure sensitivity, the possible orientations of single crystal surfaces span a continuous 2D space. Comprehensive study of these phenomena requires high throughput methods that allow rapid, concurrent measurements of surface composition and chemistry across parameter space.

Composition spread alloy films (CSAFs) have been used as sample libraries for accessing broad and continuous alloy composition spaces. CSAFs are thin alloy films deposited on appropriate substrates such that they have lateral composition gradients. A binary CSAF of components A and B can run from pure A at one end to pure B at the other. A ternary CSAF can be prepared with a triangular region that mimics a ternary composition diagram and literally contains all possible ternary alloy compositions. These alloy sample libraries are ideal for the study of surface segregation. We have used low energy He^+ ion scattering to map segregation at 100s of alloys spanning the composition spaces of CuPdAu, CuAgAu and NiPdAu ternaries. This work has explored both equilibrium segregation over a range of temperatures and the measurement of surface segregation kinetics.

Surface Structure Spread Single Crystals (S^4Cs) have been used as sample libraries for accessing broad and continuous ranges of single crystal surface orientations. S^4Cs are metal single crystal disks fabricated such that one side is a section of a sphere. These usually (but not necessarily) have a low Miller index plane exposed at their center and the rest of the surface exposing all possible surfaces orientations lying within some polar angle (14^o in our case) of the low Miller index point. By first adsorbed reactive species on the curved surface and then spatially mapping their coverage versus time, $\vartheta_{hkl}(t)$, at a given temperature we are able to extract reaction rate constants as functions of surface orientations. In this manner, we have studied the enantiospecific decomposition kinetics of D- and L-tartaric acid on all chiral Cu(*hkl*)R&S surfaces vicinal to the three low Miller index planes.

9:20am **SS1+HC-WeM-5 Unveiling the Ability of Rh Single Atoms to Enhance the Dissociation of Molecular Oxygen and Spillover to Cu**, ***Volkan Cinar***[1], Tufts University*; D. Guo,* Washington State University, US*; Y. Wang, C. Easton, H. Chen,* Tufts University*; N. Ulumuddin,* Washington State University, US*; R. Hannagan,* Tufts University*; I. Waluyo,* Brookhaven National Laboratory*; J. McEwen,* Washington State University, US*; C. Sykes,* Tufts University

Copper-based catalysts are used in a wide range of heterogeneous catalytic processes such as methanol synthesis, CO oxidation, epoxidation of alkenes, and the water-gas shift reaction. As many of these reactions can take place in oxidizing environments, CuO_x surfaces have been extensively studied to better understand structure-function relationships. Single-atom alloys (SAAs) are a new type of catalyst in which small amounts of reactive dopants (Pd, Pt, Ni, Rh, etc.) are present as isolated atoms in less reactive metals such as Cu. However, literature of the behavior of these materials under oxidizing conditions is limited.

Using surface science experiments we discover that 0.005 monolayers Rh in the surface of Cu(111) enhances the rate of O_2 dissociation by ~20 times. TPD experiments are conducted using the partial oxidation of methanol to formaldehyde to titrate away the adsorbed oxygen and hence quantify the increased dissociative sticking probability of O_2 on the RhCu SAA vs. Cu(111). CO "poisoning" and annealing experiments were conducted to further investigate the role of the Rh atoms in dissociating molecular oxygen. These TPD experiments reveal that adsorption of ~1% of a monolayer of CO, which block the Rh sites and reduce the O_2 dissociation back to pure Cu(111) providing evidence that Rh is the site for O_2 activation. Furthermore, annealing the surface to 250°C, which induces the subsurface diffusion of Rh, gives the same result. Further quantification of oxygen uptake on the RhCu SAA reveals a spillover effect whereby molecular oxygen dissociates on the Rh atom sites and diffuses to sites on Cu(111). STM experiments are performed to elucidate the atomic-scale detail of this effect. The STM images reveal that on Cu(111) and the RhCu SAA, oxidation occurs at the Cu step edges, consistent with literature reports. However, for the case of the RhCu SAA, we observe features on the terraces, consistent with atomic oxygen spill over from Rh atoms. Our DFT calculations quantify the energetics of the process showing that the molecular oxygen binds to the Rh sites stronger than Cu(111) and that the activation barrier is lower as compared to bare Cu(111). Furthermore, our DFT results support the spillover of oxygen atoms from Rh site to the Cu host. Together, these results begin to shed light on the role of single metal atom dopants in promoting Cu oxidation.

Surface Science Division
Room 319 - Session SS2+AS+HC-WeM
Nanoparticle Surfaces

Moderator: Zdenek Dohnalek, Pacific Northwest National Laboratory

9:40am **SS2+AS+HC-WeM-6 Understanding the Growth of Sn and Pt-Sn Clusters on Titania and Carbon Surfaces**, *S. Beniwal,* University of South Carolina*; W. Chai,* University of Texas at Austin*; M. Qiao, P. Kasala,* University of South Carolina*; K. Shin, G. Henkelman,* University of Texas at Austin*; **Donna Chen**,* University of South Carolina

Supported Pt-Sn bimetallic clusters have applications in number of catalytic processes, including dehydrogenation of alkanes and selective hydrogenation of unsaturated aldehydes. In these reactions, the presence of Sn is known to promote the desired selectivity of the Pt-based catalyst. However, the chemical activity the supported Pt-Sn catalysts is dependent on the Sn oxidation state and the nature of Sn interaction with the support, as well as dispersion. Sn and Pt-Sn clusters have been vapor-deposited on $TiO_2(110)$ and highly oriented pyrolytic graphite (HOPG) and studied by scanning tunneling microscopy, X-ray photoelectron spectroscopy, and low energy ion scattering. Deposition of Sn on titania results in the formation of small, uniformly sized clusters with SnO_x at the cluster-support interface and reduction of the titania support. Subsequent deposition of Pt produces exclusively bimetallic clusters, and Sn diffuses away from cluster-support, resulting in a decrease in SnO_x and Sn-rich cluster surfaces. Density functional theory (DFT) calculations demonstrate that M-TiO_2 bonding is favored over M-M bonding for M=Sn, unlike for transition metals such as M=Pt, Au, Ni, and Co. Furthermore, the substantial charge transfer from Sn to TiO_2 leads to dipole-dipole repulsion of Sn atoms that prevents agglomeration into the larger clusters that are observed for the mid-late transition metals. DFT studies also confirm that addition of Pt to a Sn cluster results in strong Pt-Sn bond formation and diminished Sn-O interactions. In the case of Sn deposition on HOPG, the clusters are surprisingly small given that Sn does not interact strongly with the support, whereas other metals such as Pt, Re and Pd readily diffuse to form large clusters that aggregate at step edges. DFT investigations show that Sn is unique in that the per atom binding energy of Sn in small clusters (<15 atoms) is as low as 0.14 eV/atom compared to Sn atoms in the bulk; for Pd, Pt, and Re, the binding energy is 0.9-1.9 eV/atom. Therefore, it is thermodynamically favorable for Sn to form small clusters and for other metals to form large clusters.

11:00am **SS2+AS+HC-WeM-10 Single Nanoparticle Surface Chemistry: Structure-Reactivity Relationships, Evolution During Reactions, and an Approach to Ultra-High Temperature Surface Chemistry**, *C. Lau, A. Friese, D. Rodriguez, **Scott Anderson**,* University of Utah

Nanoparticles (NPs) are inherently heterogeneous, with variations in size, shape, and distributions of reactive sites. This talk will explore the kinetics for oxidative etching of *individual* carbon and silicon NPs, tracking changes in reactivity as the NP structure evolves under reaction conditions.

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

Examples of O_2 oxidation of typical carbon black and graphene oxide NPs is shown in the figure, which shows the NP mass vs. time at 1200 K under inert (unshaded background) and oxidizing conditions (cyan background). The lower frames show how EE_{O2}(the etching efficiency in terms of Da of mass lost *per* O_2 collision) varies with the NP mass. Oxidative etching of carbon NPs varies significantly between NPs from different feedstocks, but there are also variations between NPs from the same feedstock, reflecting variations in the distributions of surface sites. Furthermore, the reactivity of individual NPs evolves non-monotonically in time as the NPs etch, with rate fluctuations of up to 5 orders of magnitude. Eventually, all carbon NPs become nearly inert to O_2, signaling that the surface layer(s) have transformed to multiwall fullerene-like structures.

For silicon NPs, we are able to study oxidation over a temperature range from 1200 to 2500 K, spanning the bulk T_{melt} of both silicon and silica. Etching involves several interacting processes that depend differently on temperature and time, thus etching of silicon-based NPs can have quite complex time dependence. For example, at temperatures (e.g. 1200 K) well below the silicon melting point (T_{melt} = 1683 K), the etching mass loss rate is initially low, accelerating as etching progresses, then eventually dropping several orders of magnitude to ~zero as the NP surface grows a passivating silica layer. At temperatures closer to the melting point (e.g. 1500 K), the oxidative mass loss rate starts high and remains high as the NP loses 15 – 30% of its initial mass, then abruptly drops to near zero as the surface passivates. For temperatures above T_{melt}, the etch rate begins to decrease immediately upon O_2 exposure, but it never drops to zero, i.e., the NP surface never passivates.

One of the features of this method is that the upper temperature possible is limited only by the sublimation rate of the particle's material. Thus for Si, it is straightforward to examine temperatures well above T_{melt}. For ultra-high temperature ceramic materials, it is possible to study surface chemistry at temperatures to well above 3000 K. Oxidation of HfC ($T_{melt} \approx$ 4200 K), will be used to illustrate this capability.

11:20am **SS2+AS+HC-WeM-11 Oxidation of Size-Selected Ag Clusters on Graphene: Bulk Motifs and Electronic Anomalies at sub-Nanoscale***, F. Loi,* University of Trieste, Italy*; M. Pozzo,* University College London, UK*; **Luca Bignardi**, L. Sbuelz,* University of Trieste, Italy*; P. Lacovig, E. Tosi, S. Lizzit,* Elettra Sincrotrone Trieste, Italy*; A. Kartouzian, U. Heiz,* Technical University Munich, Germany*; R. Larciprete,* Institute for complex systems - CNR, Italy*; D. Alfè,* University College London, UK*; A. Baraldi,* University of Trieste, Italy

The evolution of the aggregation of condensed matter from single atoms to three-dimensional structures represents an crucial topic in nanoscience since it contains essential information to achieve tailor-made growth of nanostructured materials. Such issue is particularly important in the case of the formation of nano-oxides, which have strong potentialities in heterogeneous catalysis reactions. In this respect, we investigated the oxidation of an Ag nanocluster composed of 11 atoms supported on epitaxial graphene on Ru(0001), combining synchrotron-based core-level photoelectron spectroscopy and *ab initio* DFT calculations. Our analysis indicated that a single Ag_{11} cluster can bond with up to 12 O atoms. Moreover, we evidenced that the Ag-O bonds in the nanoclusters include contribution from the Ag 4d states, with a remarkable difference with the case of Ag single crystal surfaces, for which only Ag 5s states are involved. The oxidized $Ag_{11}O_{12}$ nanocluster is indeed more similar to a bulk oxide rather than to an oxidized surface, as it reaches a final hybrid structure formed of d^{10} Ag(I) and d^8 Ag(III) ions which strongly resembles that of AgO bulk oxide. Furthermore, we found that the Ag 3d core level in the Ag_{11} nanoclusters is dominated by initial state effects and has a unique behavior when increasing the oxygen density. This anomaly seems to be related to the dimensionality of the nanocluster and provides an excellent example of the differences that sub-nanometer atomic aggregates of a material show with respect to the bulk and surface counterparts.

11:40am **SS2+AS+HC-WeM-12 Precision Engineering of Metal Nanoparticle Surfaces for Fundamental Studies of Catalytic Reactivity***,* ***Michelle Personick,*** Wesleyan University **INVITED**

Understanding fundamental structure-activity relationships in catalysis is key to enabling the directed design of improved catalytic materials, but the surfaces of working catalysts are complex. The use of precisely defined nanomaterials provides a powerful tool for facilitating insights into active site structure and reaction mechanisms. Such materials also enable testing and validation of insights from fundamental experimental and computational surface science under catalytic operating conditions. However, synthesizing nanomaterials with the precise surface structures and compositions necessary to test specific hypotheses is a significant challenge, and creative new approaches to materials synthesis are required—particularly for bimetallic materials. This talk will highlight the use of large (~75 nm), well-defined metal nanoparticles as model surfaces to test predictions from computational surface science. In addition, it will describe materials-generalizable synthetic tools developed by our research group for controlling metal nanoparticle shape, surface structure, defect structure, and composition, with an emphasis on dilute bimetallic nanoparticles. Halide-assisted metal ion reduction enables the controlled co-reduction of metals with dissimilar reactivity (Au/Pd, Pd/Cu, Au/Ag), while differentially tuning the relative rates of reduction for each metal to define the shape and surface composition of the material. Plasmon-assisted metal ion reduction takes advantage of the light-responsive properties of materials like Ag to enable (1) the directed deposition of catalytically active but poorly plasmonic metals such as Pt, and (2) the reconfiguration of monometallic Ag materials to modify defect structure while retaining the same surface structure and adsorbates. Together with other techniques developed in our research group, these tools provide a platform for the precision engineering of catalytic metal nanomaterials.

Applied Surface Science Division
Room 320 - Session AS+CA+HC+LS-WeA

Shining a Light on Surface Chemical Metrology: In Memory of Martin Seah

Moderators: Donald Baer, Pacific Northwest National Laboratory, **Alexander Shard**, National Physical Laboratory, UK

2:20pm **AS+CA+HC+LS-WeA-1 Metrology Lights the Way for Advances in Metabolic Imaging at the Single-cell Scale*, Ian Gilmore,*** National Physical Laboratory, UK **INVITED**

The international community recently paid homage to Martin Seah in a Special Issue of Surface Interface Analysis [1] with reminiscences, biographical accounts of his considerable achievements, reviews and research articles. The collection takes its title "Shining a light on surface chemical analysis" from Martin's research career of over 5 decades dedicated to guiding the community to make better measurements in traditional and emerging areas of surface chemical analysis. Where there was darkness, he brought light. Here, we begin with a retrospective look at Martin's considerable achievements in XPS, AES, SIMS, AFM and leadership in International Standardisation.

Martin was never one for too much retrospection though and was always full of energy and enthusiasm to tackle the issues of tomorrow. We therefore show how by using Martin's methodology that metrology is lighting the way for metabolic imaging at the single-cell scale, which is of critical importance in the development of new pharmaceuticals, understanding tumour heterogeneity and fundamental biological studies to understand metabolic rewiring in diseases.

References

[1] Gilmore, I.S. (2022), Martin P Seah MBE—Shining a light on surface chemical analysis. Surf Interface Anal, 54: 282-284. https://doi.org/10.1002/sia.7071

3:00pm **AS+CA+HC+LS-WeA-3 Two-Point Calibration Method for Quantifying Organic Binary Mixtures Using SIMS in the Presence of Matrix Effects*, Alexander Shard,*** National Physical Laboratory, U.K.*; A. Miisho,* Kobelco, Japan*; J. Vorng, R. Havelund, I. Gilmore,* National Physical Laboratory, U.K.*; S. Aoyagi,* Seikei University, Japan

Quantification of composition for organic mixtures is required in the analyses of technological materials from organic electronics to drug delivery systems. The molecular specificity of secondary ion mass spectrometry provides an unparalleled ability to distinguish organic materials, however it is difficult to use for quantitative analysis. In a few cases, there is a linear dependence between the composition, expressed as a ratio of component volumes, and the secondary ion intensities, expressed as a ratio of intensities of ions from each component. However, this ideal relationship fails in the presence of matrix effects and linearity is observed only over small compositional ranges, particularly in the dilute limits. We present an empirical method which introduces a power law dependence between the intensity ratio and the volume fraction ratio. A physical model of the organic matrix effect is employed to test the limits of the method and a mixed system of 3,3'-bis(9-carbazolyl) biphenyl and tris(2-phenylpyridinato)iridium(III) is used to demonstrate the method. In practice, we describe a two-point calibration, which determines both the exponent in the power law and the sensitivity factor for the conversion of ion intensity ratio into volume fraction ratio. We demonstrate that the two-point method significantly improves the accuracy of quantification compared to a one-point, linear calibration and is valid over a wide compositional range. Since the method enables the use of clearly identifiable secondary ions for quantitative purposes and mitigates commonly observed matrix effects in organic materials, the two-point calibration method could be of significant benefit to SIMS analysts.

3:20pm **AS+CA+HC+LS-WeA-4 OrbiSIMS Metrology: Optimization of Inorganic Depth Profiling using Ge and Sb Delta-layer Samples***, Y. Zhou,* National Physical Laboratory, UK*; A. Franquet, V. Spampinato,* IMEC, Belgium*; A. Pirkl,* IONTOF GmbH, Germany*; W. Vandervorst, P. Van Der Heide,* IMEC, Belgium*;* ***Ian Gilmore,*** National Physical Laboratory, UK

In 2017, NPL introduced the 3D OrbiSIMS instrument [1] for sub-cellular resolution molecular imaging with high-mass resolution and mass accuracy (> 240,000 at m/z 200 and < 2 ppm, respectively). Since then, IONTOF installed multiple Hybrid SIMS systems around the world with a growing range of applications, largely in, but not limited to, the life-sciences.[2,3] The dual ToF-MS and Orbitrap-MS analyzers combined with Bi liquid metal, gas cluster, and low energy $O_2^+$and Cs^+ ion beams provide a highly versatile platform for materials science studies.

Since the Orbitrap-MS is designed to operate with a continuous ion source, the instrument is well configured to take advantage of single ion beam depth profiling approaches. For example, Sul et al[4] recently demonstrated the ability to sputter depth profile a blue phosphorescent OLED device using GCIB sputtering with Orbitrap-MS. Similarly, Spampinato used the high-mass resolving power of the Orbitrap-MS to study thin EUV photoresist films where ToF-SIMS suffered from severe molecular interferences. [5] Moreover, there is growing interest in the application of the OrbiSIMS to inorganic semiconductors. Franquet et al[6] recently showed how the high mass resolution of the Orbitrap-MS analyzer combined with 2 keV Cs^+ sputtering enabled the composition of SiGe architectures down to < 20 nm to be determined with improved accuracy using the Self Focusing SIMS methodology.[6]

In this study, we use a sample consisting of 8 Ge delta-layers with a spacing of 4.8 nm in a silicon matrix. The thickness of each delta-layer is ~0.2 nm with a concentration of below 1 atom%. A second sample consisting of 5 Sb delta-layers with a spacing of 10 nm in a silicon matrix was also used. A sputter gun using either O_2^+or Cs^+ between 1 keV and 2 keV was used for both sputtering and analysis with Orbitrap-MS detection. The optimization of instrument parameters including sputter rate, injection time and sputter beam energy on the depth resolution ($\lambda_{g,}\lambda_d$ and Gaussian broadening)[7]will be discussed.

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4:20pm **AS+CA+HC+LS-WeA-7 Complementary Perspectives on the Impacts of Martin Seah on Surface Analysis*, Don Baer,*** Pacific Northwest National Laboratory **INVITED**

Throughout his more than four decade career Dr. Martin Seah had a major impact on quantitative surface analysis and the surface analysis community. There were many facets to his activities, interactions, and leadership and most of those who interacted with him knew only a portion of his many contributions. This talk will describe ways that he impacted my career and some of the activities that may have been less visible to many in the surface analysis community. Accurate quantitative surface analysis was a theme throughout his career. My introduction to his work was associated with measurements of the segregation of trace elements to the grain boundaries of metals and metal alloys.In the 1970s understanding of the challenges to quantitative analysis of electron spectroscopy was evolving and results were often inconsistent and sometimes a source controversy. Work by Seah and Hondros was important to put these measurements on a sound foundation. An important trait of Martin's work was his ability to identify needs or information gaps and to proceed to fill them.There are many examples of this, including application of XPS to measure very thin oxide films on silicon wafers, simple models of electron mean free path lengths, models for understanding sputtering rates of cluster ion sources and the development of consistent terminology for surface methods and analysis. Martin made significant and enjoyable efforts to communicate information to the community and offered encouragement to other researchers in a variety of ways.Although his presentations seemed to be spontaneous and often full of humor, they were always well thought out and delivered clear and important messages. In viewing one of my presentations the year of his death, he made many complementary remarks in email correspondence, but chided me for having too much information on my closing slide.He said that it was important to have a simple clear final message for each talk. A portion of his influence and success was due to many delightful professional and informal social interactions.When he liked a presentation, he would offer a simple "well done" and I very much valued such comments when I received them.At an American Chemical Society Meeting in New York City we went to the half price theatre ticket booth and chose to attend not a Broadway musical but a delightful Arthur Miller play with almost no audience.

5:00pm **AS+CA+HC+LS-WeA-9 The 'Crypto-Electron' Question: XPS of Tribo-electrified Insulators*, Hagai Cohen,*** Perlman bdg., The Weizmann Institute, Israel

Recent experiments on tribo-electrification have raised fundamental questions on the role of electrostatic charge in chemical and physical surface activity. Cryptolectrons were claimed to be created and, subsequently, be exploited to establish 'single-electrode electrochemistry'. However, our XPS study of this problem reveals methodological issues that were not taken into account. I will show that XPS proposes an interesting template for studies of various processes under controlled surface charge conditions, with which limiting factors on the magnitude of electrostatic surface fields can be extracted. How would a cryptoelectron, if existing, look like and can XPS imitate this creature to some extent – these questions and related ones will be discussed.

5:20pm **AS+CA+HC+LS-WeA-10 Effects, in XPS, on Composition Determination Using Different Background Removal Procedures: Single Crystal Fe_2O_3 as an Example*, Christopher R. Brundle,*** C R Brundle and Associates*; B. Crist,* xpsdata*; P. Bagus,* University of North Texas

Precision achievable in XPS is very good. Accurate quantitation from relative peak intensities is more difficult, even for homogenous materials. Normalizations for σ and λ are required, but the procedures are by now well understood. The accuracy of removing a background to establish the intrinsic spectrum is on less secure ground. There are several approaches, and implementation requires adjustment of parameters either manually, or automatically by the software used. The situation is at its most unsure when an XPS core level "peak" consists of overlapping structure spread over a wide (up to several 10's ev) BE range, such as with Fe 2p (multiplet splitting; shake structure) and O1s (shake) in Fe_2O_3 (1). The situation is similar for many other transition metal compounds. We examine, for a hematite single crystal, Tougaard and Shirley based background removals. Our conclusion is that the high BE endpoint, ie. where the person taking, or analyzing, the data sets the background to meet the experimental spectrum (implying there is no further intrinsic signal beyond that BE) is critical for high composition accuracy. Obviously, theory input on where intrinsic substructure ends helps to establish what is a reasonable endpoint (1). It is quite possible to adjust endpoints (Fe2p and O1s) to return the "expected" answer, 40% atomic Fe, but this is arbitrary, and, of course, assumes 100% accuracy of the relative σ and relative λ in addition to assuming a) that the Transmission Function, TF, of the instrument has been accurately calibrated, and b) that a small signal from surface OH is properly accounted for. So, in this presentation we are more concerned with the *range in composition* returned by each method (and variations within each method), rather than absolute values, when different, but plausible, endpoints are used. We also find that results differ using high energy resolution and low resolution. The two effects together amount to a ~4% variation in determined Fe %age for Tougaard and ~6% for Shirley. We stress that this work represents a practical approach, using the particular versions of the Tougaard and Shirley software available with the instrument involved, and no sample treatment within the instrument, which we believe is the way most practical XPS analyses are actually performed. Finally, we discuss the reasons for the differences observed and examine other possible procedures.

1) Origin of the complex main and satellite features in Fe 2p XPS of Fe_2O_3, Paul S. Bagus, Connie J. Nelin, C. R. Brundle, B. Vincent Crist, N. Lahiri, and Kevin M. Rosso, PCCP 2022 and references therein.

5:40pm **AS+CA+HC+LS-WeA-11 XPSOasis.org: the XPS Peak-Fitting Network*, Alberto Herrera-Gomez,*** CINVESTAV, Mexico*; D. Herrera-Rendon, E. Aguilar-Diaz,* RDATAA, Mexico

The XPSOasis Web platform aims to make available to the XPS community, free of charge, tools that facilitate communication between XPS users; this includes discussion forums, peak-fitting databases (one for each core-level), dynamic communication between users, and free data analysis software. The web platform allows users of different fitting software to easily upload posts to ask questions with images of the fitting that concern them. To answer the questions, the posts contain the data, allowing knowledgeable users to download and work on the recommendations.Novice users can consult expert users in direct conversations. Technical discussions on the analysis of XPS data can also be held.

To hook expert (and non-expert) users, the participation is rewarded with *Spicer* points, which are accumulated through *likes* in their posts (given by other users) and when one of their posts reaches the peak-fitting data base (which is a decision of the corresponding moderator).Categories are defined in terms of the points.User belonging to certain categories can compete to become moderators of a certain core-level forum and database.They could also offer courses.Another advantage of having posts in the database is that they become the norm and could be cited.

The usefulness of XPSOasis.org is a function on the availability of peak-fitting parameters for each core-level for each element under a variety of chemical environments.Since it is a user-based platform, it becomes more useful as the number of users posts increases.This is a possible solution (which will, in fact, be provided by the XPS community itself) for the erroneous XPS analyses all too common in the scientific literature.

6:00pm **AS+CA+HC+LS-WeA-12 ASSD Peter Sherwood Mid-Career Award Talk: Advancing X-ray Photoelectron Spectroscopy (XPS) Methodologies for Materials Research*, Mark Biesinger*[1]**, Surface Science Western, Canada **INVITED**

Chemical state X-ray photoelectron spectroscopic (XPS) analysis of first row transition metals and their oxides and hydroxides is challenging due to the complexity of the 2p spectra resulting from peak asymmetries, complex multiplet splitting, shake-up and plasmon loss structure, and uncertain, overlapping binding energies. Our work has shown that all the values of the spectral fitting parameters for each specific species, i.e. binding energy (eV), full width at half maximum (FWHM) value (eV) for each pass energy, spin-orbit splitting values and asymmetric peak shape fitting parameters, are not all normally provided in the literature and databases, and are necessary for reproducible, quantitative chemical state analysis.

We have worked toward a consistent, practical, and effective approach to curve fitting based on a combination of 1) standard spectra from quality reference samples, 2) a survey of appropriate literature databases and/or a compilation of literature references, 3) specific literature references where fitting procedures are available and 4) theoretical fittings, where available, of multiplet split reference spectra. The use of well characterized standard samples and fitting of the entire peak shape has been shown to increase our ability to accurately identify and (semi) quantify the various species present in mixed oxide/hydroxide systems [1,2,3]. Additional chemical information has also been elucidated from Auger parameters and by using Wagner plots [4,5]. The unique spectral shapes of the LMM Auger peaks for these transition metals, particularly for Cu [5], have also been shown to be of use for chemical speciation. These methods have been shown to be effective in a wide variety of applications.

An overview of these curve-fitting methodologies will be presented along with examples highlighting how these methods have been used to elucidate complex sample chemistries.A recent assessment of available charge corrections procedures for insulating samples will also be shown [6].

References:

1. M.C. Biesinger, et al., *Surf. Interface Anal.***41** (2009) 324.
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3. M.C. Biesinger, et al., *Appl. Surf. Sci.***257** (2011) 2717.
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5. M.C. Biesinger, *Surf. Interface Anal.***49** (2017) 1325.
6. M.C. Biesinger*, Appl. Surf. Sci*. **597** (2022) 15381.

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-WeA

Bridging Gaps II: Single Atom Alloys and Desirable Defects

Moderators: Rachel Farber, University of Chicago, **Gareth Parkinson**, TU Wien, Austria

3:00pm **HC+AS+SS-WeA-3 Atomic-Scale Structure-Function Relationships of Pt-based Copper Oxide Single-Atom Catalysts*, Audrey Dannar,*** *A. Schilling, G. Giannakakis, A. Therrien, E. Sykes,* Tufts University

Single-atom catalysts comprised of isolated metal atoms anchored on oxide supports have recently gained considerable attention for their potential to

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[1] **ASSD Peter Sherwood Award**

improve the activity and or selectivity of important industrial reactions. We have previously shown that single Pt atoms on a copper oxide thin-film are able to perform low-temperature CO oxidation without sintering, a common deactivation mechanism of single-atom catalysts. Using a combination of scanning tunneling microscopy, infrared and x-ray photoelectron spectroscopy, and temperature programmed desorption we elucidated the atomic-scale surface structure of these model catalysts and related that structure to catalytic function. We found that Pt atoms have a preferred binding site on the oxide surface and that they can oxidize CO, but not H_2. These fundamental surface results were leveraged in the design of nanoparticle analogs that were active and selective for the preferential oxidation of CO. In order to extend this approach to bulk oxides we have begun characterizing the 111 facet of a Cu_2O single-crystal which better mimics the Cu_2O particles present in high surface area catalysts. Scanning tunneling microscopy images of the $Cu_2O(111)$ surface reveal atomic-scale structures that may be responsible for the reactivity observed in real catalysts. Low-energy electron diffraction patterns reveal reconstructions in the model catalyst surface induced by exposure to reducing or oxidizing conditions, which is important in terms of how the active sites, and their coordination to the oxide support evolve under relevant reaction conditions. Taken together, our thin-film and bulk copper oxide surfaces decorated with isolated Pt atoms provide useful model systems with which to parse out atomic-scale structure-function relationships that inform the rational design of novel catalysts.

4:20pm **HC+AS+SS-WeA-7 Comparison Study of Several Transition Metals on Two Different TiO_2 Model Supports: Anatase TiO_2 (101) and Rutile TiO_2 (110)***, **Lena Puntscher**, K. Daninger, P. Sombut,* TU Wien, Austria*; M. Meier,* University of Vienna, Austria*; M. Schmid,* TU Wien, Austria*; C. Franchini,* Alma Mater Studiorum, Università di Bologna, Bologna, Italy*; U. Diebold, G. Parkinson,* TU Wien, Austria

Single-atom catalysis (SAC) offers an opportunity to minimize the amount of precious catalyst material required for traditional heterogeneous catalysis and to “heterogenize” reactions presently requiring homogeneous catalysis; this would eliminate the problem of separating catalyst and product, while retaining the excellent selectivity and activity of homogeneous catalysts [1].

Unravelling how metal atoms bind to oxide supports is crucial for a better understanding of the SAC´s catalytic properties. Using STM and XPS, we compare the adsorption geometry and stability of several transition metals on TiO_2 model supports: anatase $TiO_2(101)$ and rutile $TiO_2(110)$ [2] and the influence of water on the dispersion of these systems.

This study points out the importance of metal-support interaction and the surprisingly different behaviour of the transition metals Pt, Rh, Ir and Ni on TiO_2 model supports.

1. Parkinson, G.S., *Single-atom catalysis: how structure influences catalytic performance.* Catalysis Letters, 2019. **149**(5): p. 1137-1146.
2. Sombut, P., et al., *Role of Polarons in Single-Atom Catalysts: Case Study of Me_1 [Au_1, Pt_1, and Rh_1] on TiO_2 (110).* arXiv preprint arXiv:2204.06991, 2022.

4:40pm **HC+AS+SS-WeA-8 Boron Effect Improves Catalytic Performance on Supported Pt/SiO_2 Catalysts for Dry Reforming of Methane at Reduced Temperatures***, **Carly Byron**,* University of Delaware*; M. Ferrandon, A. Kropf,* Argonne National Laboratory*; S. Bai,* University of Delaware*; M. Delferro,* Argonne National Laboratory*; A. Teplyakov,* University of Delaware

Metal nanoparticles supported on metal oxides are studied as catalysts for a variety of applications, most notably catalytic hydrocarbon reforming reactions. Platinum has shown to be a highly active catalyst for the dry reforming of methane (DRM), which converts CO_2 and CH_4 into “synthesis gas”, which can be further processed to produce biofuel. However, the DRM process requires further optimization before large scale use. Our prior studies have shown that boron has a positive effect on platinum/silica catalyst for butane dehydrogenation, due to the reduction in carbon contaminant (coke) on the surface and migration of carbon deposit away from platinum active sites. Based on these findings, $Pt/B/SiO_2$ catalysts were prepared for DRM catalysis and compared with Pt/SiO_2 catalysts without boron promotion. Both catalysts had similar concentrations of platinum, but the catalytic activity after 14 hours for boron-containing catalyst was drastically improved, resulting in nearly 100% CO_2 conversion compared to 12% without boron. The reacted catalysts were investigated with synchrotron x-ray adsorption spectroscopy (XAS), transmission electron microscopy (TEM), x-ray electron spectroscopy (XPS), and Raman spectroscopy to identify the deactivating factor. It was determined that neither sintering nor coking was a significant factor in Pt/SiO_2 catalyst deactivation, instead that platinum and boron interact electronically to optimize DRM catalysis, which results in high activity at relatively low DRM operating temperatures.

5:00pm **HC+AS+SS-WeA-9 Facet Dependence of RhCu Single-Atom Alloy Structure and Reactivity***, **Yicheng Wang**, R. Hannagan,* Tufts University*; J. Schumann, M. Stamatakis,* University College London, UK*; C. Sykes,* Tufts University, UK

Direct propane dehydrogenation is a promising way to address the current propene shortage. RhCu single-atom alloys (SAAs), predicted by first-principal calculations, have recently been demonstrated to be efficient propane dehydrogenation catalysts. While RhCu model catalysts have been conducted on the (111) facet of Cu to understand the C-H activation mechanism, other facets have not been explored which is important fundamental information needed to bridge the structure gap between model catalyst and nanoparticle studies. In order to better understand the effect of the more open (100) facet, we investigated the RhCu(100) SAA surface using a combination of scanning tunneling microscopy (STM), temperature programmed desorption (TPD), reflection absorption infrared spectroscopy (RAIRS) and density functional theory (DFT). Our STM results reveal a striking difference between the alloying mechanism of Rh atoms in Cu(111) versus Cu(100) surface facets.Unlike RhCu(111) where Rh atoms tend to form dense brim in the regions above the step edges, homogeneously dispersed Rh atoms can be observed across the whole Cu(100) surface. DFT modeling indicates that the starkly different Rh distribution can be attributed to the different alloying mechanisms between the Cu(111) and Cu(100) where Rh atom place exchange into the terraces is facile on Cu(100). CO TPD and RAIRS experiments were conducted to study the Rh active sites in the RhCu(100) alloys. CO TPD experiments revealed CO desorption at both low and high temperature hinting at the existence of dicarbonyls, which had not previously been observed on SAAs. RAIRS was used to demonstrate that the low temperature peak corresponded to the transition from dicarbonyls to monocarbonyls and the high temperature peak involved the desorption of the monocarbonyls, which was further confirmed by DFT. Together, these results help us to understand the active sites in RhCu(100) SAAs and the influence of the coordination environment on the binding to Rh sites. These results will further shed light on the structural characterization of high surface area SAA catalysts.

5:20pm **HC+AS+SS-WeA-10 Crossing the Great Divide Again: Psuedo-Molecular Beams at Atmospheric Pressure***, E. High, **Christian Reece**,* Harvard University

In order to reliably predict catalytic activity, we require accurate and robust kinetic models. Fundamental surface science studies on model catalysts are generally considered the “gold standard” for measuring in-depth kinetic and mechanistic information. However, there is often a perceived difficulty in transferring this knowledge from ultra-high vacuum surface science to applied reactor conditions i.e., at elevated temperature and pressure. This misunderstanding led to the development of terms such as pressure gap. In reality this so-called pressure gap is in fact a pressure continuum, with the caveat that the catalyst state (i.e., the structure and composition) must be kept consistent across the pressure regimes [1,2]. Herein we demonstrate a high-pressure analogue to classic molecular beam experiments utilising a home-built transient flow reactor in order to directly compare results measured at UHV and at atmospheric pressure. Using CO oxidation over polycrystalline Pd as a test reaction, we find that the transient behaviour observed at UHV [3] is recreated in the transient flow reactor. Further, the fundamentally derived kinetic model that is used to describe the molecular beam experiments also recreates the transient behaviour observed at atmospheric pressure when fed into a packed bed reactor simulation.

[1] Reece, C., Redekop, E.A., Karakalos, S., Friend, C.M. and Madix, R., 2018. Crossing the great divide between single-crystal reactivity and actual catalyst selectivity with pressure transients. Nature Catalysis, 1(11), pp.852-859.

[2] Reece, C. and Madix, R.J., 2021. Moving from Fundamental Knowledge of Kinetics and Mechanisms on Surfaces to Prediction of Catalyst Performance in Reactors. ACS Catalysis, 11(5), pp.3048-3066.

[3] Libuda, J., Meusel, I., Hoffmann, J., Hartmann, J., Piccolo, L., Henry, C.R. and Freund, H.J., 2001. The CO oxidation kinetics on supported Pd model catalysts: A molecular beam/in situ time-resolved infrared reflection absorption spectroscopy study. The Journal of Chemical Physics, 114(10), pp.4669-4684.

5:40pm **HC+AS+SS-WeA-11 Self-Propagating High Temperature Synthesis of Chevrel Phase Sulfides from Elemental Precursors***, **Tessa Gilmore**, M. Pawar, P. Gouma,* The Ohio State University

Self-propagating high temperature synthesis (SHS) is a spontaneous, irreversible, combustion process that requires close to no energy to produce complex materials at high temperature through self-sustained reactions. Little is known about the mechanistic nature of this versatile process, which limits its controllability and applicability. Chevrel Phase (CP) compounds (MxMo6S8-CPs) constitute a class of multifunctional, ceramic, designer materials targeted for catalysis, battery electrodes, quantum computing, and other applications. In this research, the successful and rapid processing of the sulfide Chevrel compound Cu4Mo6S8 via SHS is demonstrated, and a mechanism is provided. Thermochemical measurements identify an atypical behavior for this SHS process where the overall reaction temperature does not surpass that of the materials with the lowest melting point. This result is attributed to intercalation assisted massive phase transformation facilitated by the use of a MoS2 precursor. Further work to synthesize the Chevrel phase using other cations is continuing.

6:00pm **HC+AS+SS-WeA-12 Growth and Activity of Ni Catalysts Supported over Ti-doped Ceria from Single Crystal Thin Films to Nanocrystals***, J. Miao, T. Ara, **Jing Zhou**,* University of Wyoming

Ceria-supported nickel catalysts have been of great interest in many important applications such as dry reforming of methane (DRM).[1] They can exhibit promising catalytic behavior owing to the unique redox properties of ceria as well as strong metal-support interactions. To enhance the thermal stability of ceria as well as improve its redox properties as a catalytic support for practical applications in catalysis, metal dopants such as Ti can be introduced into ceria. Our previous studies have shown that well-ordered (111)-oriented $Ce_{1-x}Ti_xO_{2-\delta}$ thin films can be prepared by simultaneous introduction of Ce and Ti onto Ru(0001) at 700 K in an oxygen environment.[2] The incorporation of Ti in ceria causes the partial reduction of Ce from +4 to +3 state. The films are of high quality consisting of flat terraces with surface features of ceria lattices, oxygen vacancies, Ti dopants, as well as domain boundaries. The extent of the Ce reduction and the nature of the surface structure correlate with the amount of Ti dopants in ceria. Compared to pure CeO_2(111), addition of Ti dopant in $Ce_{1-x}Ti_xO_{2-\delta}$(111) can provide unique anchoring sites and interaction for deposited Ni, which can significantly stabilize Ni as smaller particles upon heating.[3] To study as practical catalysts, powder materials of 5 wt.% Ni dispersed over a series of $Ce_{1-x}Ti_xO_{2-\delta}$ (x: 0-0.5) were prepared using sol-gel and impregnation methods and investigated for the DRM reaction with a fixed-bed flow reactor, monitored by on-line mass spectrometer and GC instruments. Incorporation of Ti into the ceria lattice forming $Ce_{1-x}Ti_xO_{2-\delta}$ was observed with Ti/Ce ratios less than 3/7 and NiO is formed over these supports. The formation of segregated titania domains was also detected in $Ce_{1-x}Ti_xO_{2-\delta}$ with higher Ti/Ce ratios ($Ce_{0.6}Ti_{0.4}O_{2-\delta}$ and $Ce_{0.5}Ti_{0.5}O_{2-\delta}$). Both NiO and $NiTiO_3$ can be formed in these Ti-rich ceria supports. Our results demonstrate that doping Ti can enhance the reducibility of ceria and tune the Ni-support interaction, which result in an enhanced coke resistance and catalytic performance of Ni in DRM. The research is sponsored by the Carbon Engineering Initiative from School of Energy Resources at the University of Wyoming.

[1] Z.Y. Liu, D.C. Grinter, P.G. Lustemberg, T.-D. Nguyen-Phan, Y. Zhou, S. Luo, I. Waluyo, E.J. Crumlin, D.J. Stacchiola, **J. Zhou**, J. Carrasco, H.F. Busnengo, M.V. Ganduglia-Pirovano, S.D. Senanayake, J.A. Rodriguez, *Angew. Chem. Int. Ed.***55, (26)**, 7455-7459 (2016).

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Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 321 - Session HC+AS+SS-ThM

Bridging Gaps III: Combined Theory and Experiment in Catalysis

Moderators: Liney Arnadottir, Oregon State University, **Sharani Roy**, University of Tennessee Knoxville

8:00am **HC+AS+SS-ThM-1 Mechanistic Understanding and Catalyst Design for Selective Methane Activations*, Ping Liu,*** Brookhaven National Laboratory **INVITED**

The development of variable catalysts to promote the activation of methane and control the conversion selectivity has long been a challenge in catalysis. One of the obstacles is the lacking in fundamental understanding of reaction network due to the complexity. Here, the mechanistic study of methane activation to carbon monoxide and/or methanol on metal/oxide and oxide/oxide will be presented using combined Density Functional Theory and kinetic Monte Carlo simulation. Our results not only provide new insight into the mechanism and active sites, but also highlight the importance of confined active site in tuning the binding of intermediates and promoting the catalytic performance.

8:40am **HC+AS+SS-ThM-3 A First Principles Study of Propane Dehydrogenation Reactions on Hydroxyl-Terminated Al_2O_3 Decorated Platinum Surfaces*, Sumandeep Kaur,*** *H. Nguyen, L. Árnadóttir,* Oregon State University

Propylene is precursor of many complex chemicals such as polypropylene, propylene oxide, acrylonitrile etc. which are used in the fabrication of numerous consumer and industrial products. Catalytic dehydrogenation of propane has been proposed as a practical route for propylene production and metal catalysts such as Pt, Pd and Sn have been extensively employed for this purpose. Recent experimental studies have shown that tailoring metal-active sites with atomic layer deposition (ALD) can increase the selectivity of propane dehydrogenation (PDH) towards propylene.[1] Herein we use DFT and microkinetic modeling to study PDH on Pt surfaces covered with Al_2O_3 to investigate the effect of ALD on PDH. Our primary results show that alumina ALD covers 1/6 of the planar surface Pt(111) blocking all the active sites for propane dehydrogenation while on the step or kink surfaces, (Pt(211), Pt(321), Pt(533)) alumina ALD forms a one-dimensional ribbon like structure along the step or kink atoms, leaning over the lower terrace and leaves room on the upper terrace for the reaction intermediates to interact with the ALD layer and the metal catalyst. These studies on PDH reactions on ALD covered Pt can lead to better understanding on how ALD can be used to tailor catalytic active sites and improve selectivity.

[1] Lu et al. ACS Catal. 2020, 10,23, 13957

9:00am **HC+AS+SS-ThM-4 Atomic-Level Studies of C_2H_4 on clean and Rh_1-Decorated $Fe_3O_4(001)$*, Panukorn Sombut,*** *L. Puntscher, C. Wang, M. Ulreich,* TU Wien, Austria*; M. Meier,* University of Vienna, Austria*; J. Pavelec, Z. Jakub, F. Kraushofer, M. Schmid, U. Diebold,* TU Wien, Austria*; C. Franchini,* University of Vienna, Austria*; G. Parkinson,* TU Wien, Austria

The local binding environment of metal-oxide supported single-atom catalysts (SACs) determines how reactants adsorb and therefore plays a decisive role in catalysis. Here, we study how $Fe_3O_4(001)$-supported Rh_1 adatoms interact with ethylene (C_2H_4) using density functional theory, combined with temperature-programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) techniques. C_2H_4 is the simplest alkene molecule, and thus a model reactant for hydrogenation and hydroformylation reactions. Our study begins with the clean $Fe_3O_4(001)$ surface[1], where C_2H_4 binds weakly. We identify and model different molecule orderings at different coverages that agree nicely with STM images, as well as explain the experimental TPD data. Then, we study C_2H_4 adsorption at 2- and 5-fold coordinated Rh sites at the $Fe_3O_4(001)$ surface, and show that the local environment has a strong effect on the adsorption properties: 2-fold Rh can adsorb two C_2H_4 molecules, while 5-fold Rh can only host a single C_2H_4 molecule. Finally, we investigate coadsorption of C_2H_4 with CO, a vital step towards enabling the hydroformylation reaction, and show that this is feasible only at 2-fold coordinated Rh sites.

1. Bliem, R. *et al.* Subsurface cation vacancy stabilization of the magnetite (001) surface. *Science* **346**, 1215–1218 (2014).

9:20am **HC+AS+SS-ThM-5 How the Support Dictates the Reactivity of FeO_x-Based Single-Atom Catalysts*, Matthias Meier,*** TU Wien, Austria **INVITED**

Single-atom catalysts are often supported by cheap oxides, such as iron oxides. As a model system[1], magnetite (Fe_3O_4), specifically its (001) facet has been used because it offers stable sites for single-atom adsorption up to high temperatures[2]. Here, I will demonstrate how important the support is for the stability of single-atoms, as well as their catalytic properties.

Rh and Ir single-atoms utilize Fe vacancies in the subsurface of the reconstructed $Fe_3O_4(001)$ unit cell to incorporate into the surface layer. Changing the positions of Fe atoms in the support as part of the incorporation process enables the single-atoms to be accommodated in a more favorable configuration than if they were adsorbing on top of the surface. Their catalytic properties are drastically affected by changes in the atomic environment. Incorporation temperatures vary depending on both coverage and the presence or absence of adsorbates, such as CO.

Changes in the support can affect not only ground states, but also reaction mechanisms and activation barriers. Pt single-atoms become mobile upon CO adsorption, forming dimers, which oxidize CO via a Mars van Krevelen reaction using a surface oxygen atom[3]. The support is temporarily altered, reducing overall activation barriers and permitting CO oxidation otherwise inaccessible at the observed experimental temperatures.

Similarly, subsurface vacancies are also present in $Fe_3O_4(111)$, modifying electronic surface states and allowing again for easy incorporation of single-atoms already at low temperatures, in line with experimental observations.

References

[1] R. Bliem, E. McDermott, P. Ferstl, M. Setvin, O. Gamba, J. Pavelec, M. A. Schneider, M. Schmid, U. Diebold, P. Blaha, L. Hammer, and G. S. Parkinson, Science **346**, 1215 (2014). [2] R. Bliem, R. Kosak, L. Perneczky, Z. Novotny, O. Gamba, D. Fobes, Z. Mao, M. Schmid, P. Blaha, U. Diebold, and G. S. Parkinson, ACS Nano **8**, 7531 (2014). [3] M. Meier, J. Hulva, Z. Jakub, F. Kraushofer, M. Bobić, R. Bliem, M. Setvin, M. Schmid, U. Diebold, C. Franchini, and G. S. Parkinson, Sci. Adv. **8**, 4580 (2022).

11:00am **HC+AS+SS-ThM-10 Modifying Ethane Oxidation Selectivity on the stoichiometric $IrO_2(110)$ surface through anion substitution*, Aravind Asthagiri,*** The Ohio State University **INVITED**

Selective alkane conversion to high value fuels or chemicals, such as methanol or ethylene, has drawn increasing interest due to abundance of natural gas. Recently, we reported a combined temperature programmed reaction spectroscopy (TPRS) and density functional theory (DFT) study of below room temperature (T ~ 120 K) activation of methane on the stoichiometric $IrO_2(110)$ surface under ultrahigh vacuum (UHV) conditions. Subsequent work also showed that ethane to ethylene selectivity could be increased on $IrO_2(110)$ by creating some proportion of hydrogenated bridging oxygen (O_{br}-H) sites, which limit the oxidative capacity of the surface. This past work suggests that substitution of O_{br} sites with inert species may be an avenue to control selectivity between full and partial oxidation. We have used DFT to explore the effects of Cl substitution of O_{br}. Chlorine is isoelectronic to O_{br}-H and selective Cl substitution of O_{br} has been demonstrated on $RuO_2(110)$ by Over and co-workers. In this work, we apply DFT to explore selective conversion of ethane on Cl-doped $IrO_2(110)$. We find that the Cl-doped $IrO_2(110)$ is still facile in converting ethane to ethylene. In contrast, the ethylene selectivity step shows a strong effect due to Cl doping. Specifically, we find that H atom transfer from ethylene to the saturated O_{br} sites is unfavorable and therefore Cl doping will promote ethylene desorption over further reaction. DFT derived microkinetic simulations show that the selectivity of ethylene peaks at ~60% Cl substitution with increasing Cl substitution reducing the reactivity of ethane. Extending this work to other halogen anion substitutions (F, Br, I) shows that Cl is the optimal dopant. While Br and I favor ethylene desorption over further reaction, these dopants decrease ethane reactivity. In contrast, F dopant does not promote ethylene desorption versus reactivity as effectively as Cl. Current efforts to develop a microkinetic model to explore ethylene selectivity under reaction conditions will be discussed.

11:40am **HC+AS+SS-ThM-12 HC Graduate Student Finalist Talk: Insight into Subsurface Adsorption and Reconstruction of Ag(111) Deduced from a Lattice-Gas Model and Monte Carlo Simulations*, Carson Mize,*** University of Tennessee Knoxville*; L. Crosby,* Joint Institute for Computational Sciences; University of Tennessee Knoxville*; E. Lander, S. Roy,* University of Tennessee Knoxville

Gas-phase surface models are a beneficial, theoretical tool for providing qualitative insight into elementary steps of surface chemistry. Elementary steps, like adsorption, play a crucial role in many chemical phenomena like surface reconstruction and industrial heterogeneous catalysis. While there exist many previously developed gas-phase adsorption models, most models are limited to low adsorbate coverages due to the computational cost required to produce high coverage models. To investigate adsorption over a broad range of adsorbate coverages on a crystalline solid, we have developed a lattice-gas adsorption model that includes surface and subsurface adsorption, tunable interaction parameters calculated with density functional theory, and larger scale modeling with Monte Carlo simulations. This model has been applied to study oxygen adsorption on a Ag(111) surface, due to experimental findings suggesting the possibility of subsurface-adsorbed oxygen species. Our first model iteration included only strongest binding sites for each region and our simulations indicated greater oxygen accumulation in the second subsurface than the first subsurface in total coverages in excess of 0.375 monolayer (ML). Our second model iteration included all high symmetry sites in each region and found the same qualitative results as the first model using canonical Monte Carlo distributions. Additionally, current grand canonical distributions suggest some subsurface oxygen adsorption exists under temperatures of 475 – 550 K and pressures of 1 – 2 bar, which are typical industrial conditions for catalysis with these systems. Our current model includes adding Ag – Ag and Ag – O interactions to model surface reconstruction, as our previous models only included the unreconstructed silver lattice. This iteration will allow us to study the role of surface and subsurface oxygen in inducing well-known surface reconstructions of Ag(111), such as p(4 × 4) and c(4 × 8) lattices, as a function of surface temperature and oxygen pressure using Monte Carlo simulations.

12:00pm **HC+AS+SS-ThM-13 Measuring and Predicting a Key Catalyst-Performance Descriptor for Supported Metal Nanoparticle Catalysts: Metal Chemical Potential*, Charles T. Campbell,*** *J. Rumptz, K. Zhao,* University of Washington

Metal nanoparticles supported on high-area oxides and carbons form the basis for many catalysts and electrocatalysts. Their activity and stability depend on both particle size and choice of support. The chemical potential of the metal atoms in the catalyst material quantifies their stability and is a convenient descriptor that captures the effects of both the nanoparticle size and the support material on both surface reactivity and sinter resistance.[1,2] This chemical potential enters quantitatively into the rate equations for sintering, making a negative contribution to the activation energy.[2] Numerous experimental and theoretical studies have also found that the stability of metal atoms in catalyst materials, including alloys, correlates with their binding energies to adsorbates, whereby surface metal atoms that are more weakly bound to the solid interact more strongly with small adsorbates like O, CO, -OH and $–CH_3$.[1-3] It is thus desirable to develop methods to predict how metal chemical potential depends on particle size and support. Herein, we report calorimetric measurements of: (1) metal chemical potential as a function of particle size and support, and (2) the adhesion energy of the solid metals to different oxide and carbon supports.From these, we have identified predictive correlations of: (1) metal chemical potential in supported nanoparticles as a function of the particle size and the adhesion energy of the particle to the support, and (2) the dependence of this adhesion energy upon the metal element in the catalyst for oxide supports.

Work supported by DOE-OBES Chemical Sciences Division.

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Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 321 - Session HC+AS+NS+SS-ThA

Special Session and Reception for the HC Community and to Celebrate Robert Madix

Moderators: Liney Arnadottir, Oregon State University, **Dan Killelea**, Loyola University Chicago, **Jason Weaver**, University of Florida

2:20pm **HC+AS+NS+SS-ThA-1 Gaede-Langmuir Award Talk: Not a Divide - A Continuum: Surface Science to Heterogeneous Catalysis***, Robert J. Madix*[1]*,* Harvard University **INVITED**

The science of surface reactivity demands control of surface structure and surface composition. Surface science methods thus enable the investigation of reactions, including oxidations, hydrogenation, and coupling, on well-characterized single-crystal surfaces by providing molecular level insight into the bond breaking and formation on surfaces that are the basis for heterogeneously catalysis. The ultimate goal of such research is to provide benchmarks for theory, forming a firm basis for *a priori* catalyst design. In the nearer term it provides a kernel of information which can be combined with theory to accurately predict rates and selectivities for extended series of analogous reactions outside the data set. In this talk, these concepts will be discussed, linking fundamental surface science studies on Au single crystals with the performance of dilute Au-based dilute metal alloy catalysts operating at elevated temperature and 1 atm pressure. The use of key surface-science methods, including XPS, vibrational spectroscopy and temperature programmed reaction spectroscopy, will illustrate the methodology for understanding catalytic reactions. This work demonstrates the ability to successfully predict surface reactivity across vast regimes of pressure, temperature and materials complexity.

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[1] **Gaede Langmuir Award Winner**

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room Ballroom A - Session HC-ThP
Heterogenous Catalysis Poster Session

HC-ThP-2 Facet-Dependent Strong Metal-Support Interaction of Pt Nanoparticles on Morphology Controlled Cu_2O Under CO Oxidation*, Seunghwa Hong*, *D. Kim,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; Y. Song,* Korea Advanced Institute of Science and Technology, Republic of Korea*; K. Kim,* Pohang Accelerator Laboratory (PAL), Republic of Korea*; J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

The strong metal-support interaction (SMSI), the interaction between metal nanoparticle and metal-oxide support, plays a central part in the catalytic behavior of catalysts, due to synergistic effects on reactivity at the metal-oxide interface. Thus, a fundamental understanding of SMSI in realistic conditions is important to the development of high-performance catalysts. However, direct investigation of SMSI is challenging, due to the structural complexity of the heterogeneous catalysts. Fac-et-controlled metal-oxide supports, such as Cu_2O, are excellent candidates for studying the SMSI at the metal and metal-oxide interface, since they possess well-defined surface structure. Furthermore, utilizing operando techniques enables in-depth characterization of the interactions at metal and metal-oxide support interfaces with a molecular level in a realistic environment.

Herein, we investigated facet-dependent SMSI at Pt nanoparticles supported on cubic and octahedral Cu_2O using surface-sensitive operando techniques. The catalytic measurement revealed facet-dependent CO oxidation activity for Pt/cubic Cu_2O and Pt/octahedral Cu_2O catalysts. Furthermore, the results of in-situ ambient pressure X-ray photoelectron spectroscopy and diffuse reflectance FT-IR spectroscopy indicate that the surface changes during the reaction depend on the facet of the support, leading to different catalytic performances. This investigation of the facet-dependent sur-face changes that significantly influence reactivity provides insight into designing high-performance catalysts via engineering the interface interaction.

HC-ThP-3 Investigation of Strong metal-support Interaction at the Pt-CoO interface Formed on Pt-Co Bimetallic Nanoparticles*, Yejin Song*, *D. Kim, S. Hong,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; K. Kim,* Pohang Accelerator Laboratory (PAL), Republic of Korea*; J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Bimetallic nanoparticles are important catalysts in heterogeneous catalysis; due to the bimetallic synergistic effect, they show higher catalytic performance than monometallic nanoparticles. Pt, a widely used catalyst, is known to alloy well with 3d transition metals (TM, e.g., Ni, Fe, Cu, and Co). In Pt-3d TM bimetallic systems, surface restructuring occurs in a variety of environments. Under oxidation conditions, Co atoms in Pt-Co nanoparticles emerged onto the surface, forming a CoO layer. Moreover, the interface between Pt and CoO enhanced catalytic activity for the Pt-Co bimetallic nanoparticle. This catalytic improvement could be explained by the strong metal-support interaction (SMSI) at the Pt-3d TM oxide interface, from the surface restructuring.

In this study, we investigated the role of the Pt-CoO interface in Pt-Co bimetallic nanoparticles during CO oxidation with surface analysis. Pt-Co nanoparticles of 4 nm were synthesized by the co-reduction method with polyvinylpyrrolidone (PVP) as a capping agent. Pt-Co bimetallic nanoparticles were supported on SiO_2 to be applied to the CO oxidation reaction. Pt-Co bimetallic catalysts exhibited higher catalytic activity than monometallic catalysts. To verify the SMSI effect at the interface of Pt-CoO in Pt-Co bimetallic nanoparticles, *operando* surface analysis, ambient pressure X-ray photoelectron spectroscopy and in-situ diffuse reflectance infrared Fourier-transform spectroscopy, were used. This study demonstrates that reaction-driven metal-oxide interface is a key factor in boosting catalytic activity.

HC-ThP-4 Effusive Molecular Beam Study of CH_4 Dissociative Chemisorption on Rh(111): The Remarkable Activity of Step Sites and Extrapolation to Catalytic Rh Films at Temperatures where Tunneling Dominates*, Xingyu Wang*, *I. Harrison,* University of Virginia

Effusive molecular beam experiments were used to measure CH_4 dissociative sticking coefficients, $S(T_g, T_s ;J)$ on a Rh(111) crystal, for which the impinging gas temperature, T_g, and surface temperature, T_s, could be independently varied, along with the angle of incidence, J, of the impinging gas. The 500 – 900 K temperature range explored is relevant to heterogeneous catalytic processes such as methane partial oxidation. A dynamically biased precursor mediated microcanonical trapping (PMMT) model of dissociative chemisorption was used to analyze the experimental results. Modelling indicates that the enhanced reactivity of step sites is not promptly poisoned on Rh(111) but rather contributes substantially to the reactivity even as high coverages of carbon accumulate at the surface. Threshold energies for dissociative chemisorption on the terraces and steps sites were optimally modeled as 74.3 kJ/mol and 36.7 kJ/mol. Translations parallel to the surface and rotations were treated as spectator degrees of freedoms. The efficacy of vibrational energy to promote reactivity relative to normal translational energy was h_n=0.55 and one surface oscillator participated in energy exchange within the collisionally formed precursor complexes. A two-channel Arrhenius model restricted to only the thermal dissociative sticking coefficient measured along the direction of surface normal, $S_n(T=T_g=T_s)$, yielded apparent activation energies of 70.6 and 25.5 kJ/mol which could be attributed to terrace and step sites, respectively. PMMT modeling of the step site reactivity on Rh(111) could be extrapolated to replicate the thermal dissociative sticking coefficient of the "defect dominated" Rh film surfaces measured by Ehrlich at temperatures in the 250 -350 K range where much of the elevated kinetic isotope effect (9 to 15) could be attributed to quantum mechanical tunneling through the reactive barrier.

HC-ThP-5 Adsorption and Decomposition of Zirconium Tetrahydroborate on Pd(111)*, Ravi Ranjan*, *M. Trenary,* University of Illinois - Chicago

Zirconium tetrahydroborate, $Zr(BH_4)_4$, is a volatile compound that has been widely used as a single-source precursor to grow carbon-free thin films of zirconium diboride by chemical vapor deposition (CVD). However, the basic surface chemistry of this compound that underlies the CVD process is largely unknown. We studied the adsorption and decomposition of $Zr(BH_4)_4$ on a Pd(111) surface with reflection absorption infrared spectroscopy (RAIRS), temperature-programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS). Palladium was chosen as the substrate as it is a good dehydrogenation catalyst. The compound was synthesized using literature methods. It was dosed onto the Pd(111) surface using standard gas-handling methods. After exposing Pd(111) at 90 K to $Zr(BH_4)_4(g)$, a RAIR spectrum was obtained that closely matched that of the pure compound, indicating that it adsorbs without dissociation at 90 K. However, upon heating to 200 K the RAIR spectrum undergoes dramatic changes indicating that a new surface species is formed that retains B–H bonds, as indicated by a B–H stretch peak at 2540 cm^{-1}. This surface species is tentatively identified as either BH_4 or BH_3 and is stable up to 300 K. Both H_2 and B_2H_6 desorb from the surface at around 175 K as observed with TPD. The decomposition of the BH_x intermediate is revealed by additional H_2 desorption peaks at 325 K and 425 K. Results obtained with XPS suggest that adsorbing $Zr(BH_4)_4$ at low temperature and then annealing does not produce ZrB_2, but instead leaves only Zr on the surface.

HC-ThP-6 Preliminary Studies of RhCu Single-Atom Alloys Using Molecular Beams*, Laurin Joseph*, *M. Powers, A. Utz,* Tufts University

A new class of heterogeneous catalysts called single-atom alloys (SAAs) combine single, isolated atoms of expensive catalytically active metals alloyed into less expensive base metals. These materials have been shown to have greater selectivity and activity relative to conventional catalysts. To date, detailed surface science studies of these materials have been limited to relatively low-barrier reactions. This work will extend the range of detailed mechanistic studies of these promising new materials to higher barrier reactions, including C-H activation. More specifically, our study focuses on the reaction of methane over a RhCu SAA catalyst. This system has been studied using reflection absorption infrared spectroscopy, temperature programmed desorption, and scanning tunneling microscopy previously.[1,2] Our lab will use supersonic molecular beam experiments to learn more about the energetic barriers and kinetics of this reaction. Presented here will be preliminary findings of these experiments as well as an explanation of the modifications made to our apparatus to make the RhCu surface.

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HC-ThP-8 Characterization of a Pt/Cu(111) Single Atom Alloy using CO-RAIRS and CO-TPD, ***David Molina***, *M. Trenary,* University of Illinois - Chicago

A combination of reflection absorption infrared spectroscopy (RAIRS), temperature programmed desorption (TPD) and Auger electron spectroscopy (AES) were used to characterize a Pt/Cu(111) single metal alloy (SAA). Carbon monoxide was used as a probing molecule to detect Pt sites in diluted alloys, down to 0.1% Pt/Cu(111) concentrations. CO-TPD spectra for known high concentrations of Pt, quantified by the ratio of the 237 MNN Pt and 920 LMM Cu Auger signals, were used for calibration for samples with Pt concentrations below the AES limit of detection. Initial RAIR spectra of CO saturated diluted alloys at 90 K have shown a signal at 2046 cm^{-1} which is overlapped with the 2078 cm^{-1} CO stretch on Cu(111) on top sites. Annealing at 180 K, above the desorption temperature of CO from Cu(111), and recooling to 90 K clearly show the 2046 cm^{-1} peak. Corresponding TPD spectra have shown desorption of CO at 345 K from the Pt/Cu(111) dilute alloys, in agreement with a previous study of CO desorption from single atom Pt sites on Cu(111). Room temperature RAIR spectra of CO on Pt/Cu(111) alloys with less than 1% Pt concentration have also shown only one vibration at 2046 cm^{-1}, assigned to CO on top of single Pt atoms. Annealing to 500 K starts diffusion of Pt to the bulk, as previously observed in Pt/Cu alloy studies.

HC-ThP-9 Surface Chemistry of Acrolein and its Hydrogenation Products on Cu(111) and Single Atom Alloy Pd-Cu(111), ***Arephin Islam***, *D. Molina, M. Trenary,* University of Illinois - Chicago

Adsorption properties and surface chemistry of acrolein and its hydrogenation products propanal, 1-propanol, and 2-propenol on Cu(111) and Pd-Cu(111) single atom alloy surfaces were studied by polarization-dependent reflection absorption infrared spectroscopy (PD-RAIRS) and temperature-programmed desorption (TPD). The experimental RAIR spectra were obtained by adsorbing multilayers of each molecule at 85 K and then annealing the surface up to 200 K to desorb the multilayer and produce the most stable monolayer structure on both surfaces. Each molecule adsorbs weakly to the surface and desorbs without reaction at temperatures below 200 K. Several TPD spectra were collected following adsorption at 85 K using similar coverages as those in the RAIRS experiments. Compared to acrolein and propanal, the two alcohols, 2-propenol and 1-propanol, have notably higher desorption temperatures and display strong hydrogen bonding in the multilayers as revealed by a broadened and redshifted O-H stretch. For acrolein, the out-of-plane bending modes are more intense than the C=O stretch at submonolayer coverage, indicating that the molecular plane is mainly parallel to the surface. In contrast, the opposite intensity trend was observed for multilayer acrolein, suggesting that the C=O bonds are tilted away from the surface. For 1-propanol, annealing the surface to 180 K disrupts the hydrogen bonding to produce unusually narrow peaks. This indicates that 1-propanol forms a highly ordered monolayer and adsorbs as a single conformer at low coverage. For 2-propenol, hydrogen bonding in the multilayer correlates with the observation of the C=C stretch at 1647 cm^{-1}, which is invisible for the monolayer. This suggests that the C=C bond is parallel to the surface for monolayer coverages of 2-propenol. Similarly, for propanal, the C=O stretch peak at 1735 cm^{-1} compared to those at 1671 and 1695 cm^{-1} is very weak for the low coverage. Still, it becomes the most prominent peak for the multilayer, indicating a change in molecular orientation. These results provided further insights into previous studies [1,2] on hydrogenation pathways of acrolein on the Ag(111) and Pd-Ag(111) SAA surface and into the challenges of selectively increasing the yield of the unsaturated alcohol.

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HC-ThP-10 Characterizing the Ag/Al_2O_3 Catalyst and Nonthermal Plasma Couple via Native OES Diagnostics, ***Ryan Chapman***, *J. Blechle,* Wilkes University

The persistently growing global demand for energy, transportation, and production will inevitably further environmental deterioration by means of hazardous emissions. Minimizing environmental damage thus requires the development of technologies that can mitigate the pollution associated with such anthropogenic sources. The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) is one of the major breakthrough technologies in the abatement of pollutants from vehicular and industrial emissions, and Ag/Al_2O_3 has been widely studied as an ideal catalyst for SCR systems due to its selectivity and tolerance to poisoning by SO_2 and water vapor. However, SCR using Ag/Al_2O_3 exhibits poor efficacy at temperatures below ~250 °C due to diminished activity of the reductant species. A promising means of overcoming these deficiencies is in the synergy between nonthermal plasma (NTP) and Ag/Al_2O_3 catalysts. Despite the potential of plasma-assisted SCR for pollution abatement as shown in the literature, the chemistry underlying the NTP/catalyst couple must be resolved to optimize the process for commercial use.

In order to further explore these synergies, optical emission spectroscopy (OES) is used to characterize a NTP ($N_2/O_2/Ar$) and Ag/Al_2O_3 couple on the basis of energy partitioning, densities, and formation/decay kinetics of relevant excited states in the plasma bulk. An inverse proportionality between NO^* density and vibrational temperature (T_v) is observed for NTP coupled with Al_2O_3 surfaces (0-10 wt% loadings in Ag). At high input powers (175-200 W), NO^* T_v's increase only marginally in the presence of 2, 5, and 10 wt% loadings, whereas a marked increase is observed in the presence of 0 wt% Ag/Al_2O_3. Even so, NO^* densities are comparably diminished (relative to the density observed at 25 W) for all systems studied. The catalytic role of Ag species in abating NO^* is further explored by the decay kinetics of NO^*. While the initial NO^* emission intensity decays with time for all NTP's coupled with substrate, the decay rate constants were greatest for bulk NTP coupled with 5 and 10 wt% Ag/Al_2O_3. Differing formation and decay behaviors of the excited states are observed with successive plasma treatments, depending on the degree of silver loading. Further investigations, such as plasma pre-treatment of the catalytic surfaces and varying surface analyses provide additional insights into the interconnected plasma-surface system. The combination of these data provide a unique insight into the mechanistic behavior and the role of the system conditions on plasma-enhanced SCR.

HC-ThP-11 Analysis of Microsilicon and Nanosilicon for Lithium-Ion Battery Anodes, ***Aaron Hsi***, *A. Sheth, C. Chu, A. Suen, S. Annamalai, S. Adibnia, M. Uddin, N. Sangeneni,* Aspiring Scholars Directed Research Program

The abundance and low cost of silicon presents the ideal candidate of silicon anodes as an energy-dense, sustainable alternative to graphite anodes in lithium-ion batteries with a reported theoretical capacity of 4200 mAh/g. However, challenges such as significant volume expansion, rapid pulverization, relatively poor conductivity, and unstable sei layers formed with the use of silicon anodes hinders the practical applications. Micro silicon and nanosilicon demonstrate promise tackling these challenges while utilizing the unique characteristic of silicon due to a larger surface area allowing for greater charge intercalation with the anode material and electrolyte without causing significant volume expansion. We have characterized micro- and nano-silicon with particle size ranges of 50 µm, 20-30 nm, and 150-200 nm through Fourier-Transform Infrared Spectroscopy (FTIR) to evaluate the presence of impurities in our samples and X-Ray Diffraction Spectroscopy (XRD) to determine the crystal structure of our samples. For electrochemical characterization, we utilized cyclic voltammetry (CV) to computationally identify the theoretical capacitance of different micro and nano-silicon-based inks (combinations of carbon black and silicon) deposited on nickel foam electrode material. Likewise we utilized Galvanostatic Charge Discharge (GCD) to identify performance characteristics of the material in battery type conditions identifying energy density, power density, and Coulombic efficiency. Our FTIR analysis indicated nano-silicon of particle sizes ranging from 20-30 nm was more prone to oxygen-related impurity formation due to a strong peak at 1071 cm-1 that corresponds to the asymmetric vibration of Si-O bonds. Through our computational analysis, we found theoretical specific capacitance values of 23.59 F g-1.of nanosilicon 01 (150-200 nm), 22.04 F g-1 of nanosilicon 02 (20-30 nm) , and 23.3 F g-1 of Microsilicon. Through testing optimal parameters of various silicon particle sizes we seek to identify the most efficient size of nano-silicon and evaluate its efficiency in an actual model lithium-ion battery utilizing COMSOL software models.

HC-ThP-12 Chemical Speciation and Structural Evolution of Rhodium and Silver Surfaces with High Oxygen Coverages*, **Dan Killelea**, E. Jamka, M. Gillum, M. Turano,* Loyola University Chicago*; L. Juurlink,* Leiden University, Netherlands

The interaction of oxygen with the surfaces of catalytically active transition metals has attracted much interest because of the relevance to heterogeneous catalysis. Recently, we have shown that oxygen coverages in excess of 1 ML are achievable using gas-phase atomic oxygen (AO) to dose the metal surfaces. This talk will discuss some recent results comparing the uptake of AO and O2 on Ag(111) to Rh(111). On Rh(111), subsurface oxygen readily forms from exposure to AO and the surface phases are dependent on the exposure temperature. We also discovered that subsurface O emerges at defects and alongside surface phase transitions. Finally, the uptake of oxygen on Ag(111) is discussed; unlike Rh(111), where little surface reconstruction occurs, Ag(111) undergoes several phase transformations as the oxygen coverage is increased. These results using AO demonstrate that UHV compatible dosing can prepare the same surfaces resulting high pressure O2 exposures, allowing for quantitative and structural analysis of the oxidized surfaces.

HC-ThP-13 Density Functional Theory Computed Descriptors for Heterogeneous Catalysis of CO_2 Sorbent Amines*, **Joshua Gabriel**,* Argonne National Laboratory, USA

Integrating carbon capture and conversion is a promising direction towards a decarbonized future for industries that are heavily dependent on carbon-based raw materials. Progress has been made in achieving the electrocatalytic reduction of carbon dioxide to carbon monoxide from CO_2 captured in a monoethanolamine solution on silver catalysts. In this work, we use density functional theory calculations to test a hypothesis that the coverage of alkali cation controls the relative binding strength of proposed species of reactants, byproducts, and products, and hence the reaction product selectivity. Our results support the hypothesis that the alkali cation affects the relative binding strength of species for CO_2 reduction and hydrogen evolution, with increased coverage favoring CO_2 reduction. This discovery provides a useful computational descriptor to better understand the process conditions that can control product selectivity in heterogeneous catalysis.

HC-ThP-14 Reactivity of Primary and Secondary Butanol Isomers on TiO_2/Au(111)*, **Haley Frankovich**, L. Garber, A. Galgano, C. Grant, E. Schell, J. Yoo, C. Rogers, J. Carmany, A. Baber,* James Madison University

Biofuels can be used to reduce global dependence on fossil fuels while contributing to a carbon neutral cycle. Biobutanol has low volatility and multiple transportation options which make it an attractive alternative fuel. Understanding the fundamental thermal catalysis processes of butanol over heterogeneous model catalysts can aid in the design of more efficient catalysts. Butanol isomers give rise to products including isobutyraldehyde, 2-butanone, butyraldehyde, isobutene, and butene, all of which have applications ranging from gasoline additives to bioplastics. For the partial oxidation of butanol isomers, TiO_2/Au(111) inverse model catalysts are promising due to their ability to catalyze redox reactions of $C_1 – C_3$ alcohols. Titania coverage effects were not reported for methanol or 2-propanol, but lower TiO_2 coverages in the presence of excess oxygen enhance selectivity of the partial oxidation of ethanol. To better understand how butanol breaks down in heterogeneous catalytic processes, temperature programmed desorption (TPD) is used to investigate its reaction. In this study, the reactivity of butanol isomers, specifically 1-butanol, 2-butanol, and isobutanol, on TiO_2/Au(111) was investigated. TPD was used to detect products and atomic force microscopy (AFM) highlighted the morphology of the surface. At low coverages of TiO_2, only 2-butanol showed expected oxidation reactivity, while, 1-BuOH exhibited low reactivity and formed reduced products, and isobutanol produced the recombinative product. At higher coverages of TiO_2/Au(111), 2-butanol formed both oxidized and reduced products, 1-butanol only formed reduced products, isobutanol produced oxidation, reduced, and recombinative products. The selectivity of the reaction was not altered during successive desorption experiments, indicating that the model catalyst was stable without reoxidation between experiments. AFM images show that the Au(111) crystal has ~0.13 ML and 0.27 ML of TiO_2 with predominantly 1D wire-like nanoparticles. Higher coverages of TiO_2 result in more particles distributed across the surface indicating that the reactivity was influenced by butanol proximity to TiO_2 nanoparticle rather than differences in size or shape.

HC-ThP-16 Synthesis and Characterization of Mixed-Ligand Monolayers on Silver Nanoparticles*, X. Wang, **William Hemmingson**, D. Green,* University of Virginia, USA

Functionalized silver nanoparticles (AgNPs) are high-value materials that have a wide variety of uses including drug delivery and catalysis. To achieve these functions, a self-assembled monolayer (SAM) of ligands is synthesized on the surface of the particle. For a mixture of ligands, it is essential to study how the ligands arrange on the surface since that can affect the properties of the system. In this study, thiolated ligands with varying chain lengths and headgroups consisting of a carboxylic acid or methyl group were synthesized and subsequently characterized using matrix-assisted laser desorption/ionization mass spectroscopy (MALDI-MS). Based on the known fragmentation pattern of AgNPs, the nearest neighbor distribution of the ligands can be determined. However, it was discovered that the fragmentation of AgNPs with carboxylic acid ligands is inconsistent at pH 7. Thus, a sodium salt solution should be added to the sample to promote cationization, which facilitates detection in MALDI-MS. Further, basic (pH=9) or acidic (pH=1) solutions have a higher yield of charged fragments than a pH-neutral sample. However, there is evidence that, under either of these conditions, the fragmentation pattern changes, and that change must be accounted for during analysis. Ultimately, this ongoing study will aid in understanding the functioning mechanisms of high-value AgNPs.

HC-ThP-17 Morphological Studies of TiO_2 Nanoparticles on Au(111)*, **Erin Schell**, J. Yoo, A. Baber,* James Madison University

TiO_2 nanoparticles (NPs) supported on Au(111) form an inverse model catalyst that is active for alcohol oxidation and reduction. To fully understand the influence that the nanoparticle size and structure have on alcohol reactivity, TiO_2/Au(111) catalysts were synthesized and characterized. TiO_2NPs were deposited on Au(111) in an O_2 background under ultrahigh vacuum (UHV) conditions. The reactivity of the TiO_2/Au(111) was tested using butanol temperature programmed reaction spectroscopy (TPRS). Two TiO_2 deposition times were studied, resulting in TiO_2 coverages of 0.13 ML and 0.27 ML, as determined by atomic force microscopy (AFM). In addition to quantifying TiO_2 coverages, the morphology and distribution of TiO_2 NPs were observed with AFM. To obtain the clearest images possible, the TiO_2/Au(111) samples were briefly annealed with a H_2 flame to clean contaminates from the surface. While a brief H_2 flame anneal does not affect the TiO_2morphology, longer flame anneals cause large changes in the morphology consistent with the formation of a mixed metal oxide. With longer TiO_2 deposition time, the TiO_2 coverage increased, but particle size remained the same. Interestingly, the higher coverage of TiO_2 resulted in more consistent reactivity with butanol isomers, whereas the smaller coverage of TiO_2 NPs showed low reactivity. AFM images suggest that the difference in reactivity is likely due to the lower number of particles rather than to differences in the size and shape of TiO_2NPs. These results help to inform the design of more active catalysts for alcohol partial oxidation.

2D Materials Technical Group

Room 303 - Session 2D+AS+BI+HC+SS-FrM

2D Materials: Biological, Electronic, Energy, and Other Applications

Moderators: Robert Hovden, University of Michigan, **Jyoti Katoch**, Carnegie Mellon University

8:20am **2D+AS+BI+HC+SS-FrM-1 Printable Electrochemical Biosensors based on 2D and 3D Graphene***, A. Ebrahimi,* ***Derrick Butler,*** *V. Kammarchedu, K. Zhou,* Penn State University **INVITED**

The increasing demand for low-cost and field-deployable biosensors has driven researchers to explore robust and scalable biochemical sensor materials and fabrication strategies. Compared to more complicated and expensive photolithography methods, printing techniques – including inkjet and direct laser writing – can enable tailorable and easily-prototypable sensors that are conducive to testing at the point of need. Electrochemical sensors have the potential to meet these criteria and integrate well with printing methods.[1] In recent years, graphene has emerged as a key material in the area of electrochemical biosensors due to high conductivity, wide electrochemical window, biocompatibility, tunability, and excellent surface sensitivity.[2] In particular, advances in preparation of solution-phase graphene suspensions (such as inks containing 2D graphene sheets) have brought about breakthroughs in printed electronics, while the advent of laser-induced graphene (LIG) has enabled the direct writing and integration of 3D porous graphene patterns in various low-cost substrates.Over the past few years, our group has developed different facile functionalization methods to enhance the sensitivity and specificity of printed devices based on graphene ink and LIG, with special attention to sensor performance in complex biological fluids (such as serum, saliva, sweat).[3,4] We have investigated application of the sensors for *in vitro* detection of small molecules involved in neurological functions, kidney disease, and wound infection as well as real-time monitoring of drug-induced response of cancer cells and biofilm biomarkers. Interfacing of the printed sensors with low-cost readout electronics and smartphone has been also demonstrated to showcase the sensor applicability for remote sensing at the point of need. Convergence of machine learning with electrochemical sensing has been also investigated, demonstrating a significant enhancement of sensitivity, while enabling reliable multiplexing of example biochemical markers in saliva and sweat. This talk will highlight our recent progress and ongoing work on advancing printable graphene biosensors in more detail.

[1] K. Yamanaka, M. C. Vestergaard, E. Tamiya, *Sensors (Switzerland)***2016**, *16*, 1761.

[2] A. Bolotsky, D. Butler, C. Dong, K. Gerace, N. R. Glavin, C. Muratore, J. A. Robinson, A. Ebrahimi, *ACS Nano***2019**, *13*, 9781.

[3] R. Muralidharan, V. Chandrashekhar, D. Butler, A. Ebrahimi, *IEEE Sens. J.***2020**, *20*, 13204.

[4] D. Butler, D. Moore, N. R. Glavin, J. A. Robinson, A. Ebrahimi, *ACS Appl. Mater. Interfaces***2021**, *13*, 11185.

9:00am **2D+AS+BI+HC+SS-FrM-3 A Large Area Selective Emitter for Thermophotovoltaic Applications***,* ***Minsu Oh****, K. Grossklaus, D. DeMeo, Z. Kranefeld, T. Vandervelde,* Tufts University

Thermophotovoltaic (TPV) devices enable energy harvesting from waste heat. In a TPV system, photons radiated by a selective emitter are converted into electricity by a photodiode due to the photovoltaic effect. The total photon flux available for power conversion is determined by the temperature, emission spectrum, and size of the emitter. Due to the engineerability of metamaterial's optical properties, they have been widely used to create TPV emitters with a desired emission spectrum for varying heat source temperatures. However, the difficulties in fabricating nano- or micrometer-sized metamaterial features that are two-dimensional over large areas pose challenges to realizing a large emitter. This fundamentally limits the output power of a TPV system due to power density restrictions. Therefore, achieving large area emitters with engineerable optical properties are critical for utility of TPV devices at scale with a reasonable power output. In this work, we experimentally demonstrate a 4-inch diameter selective emitter fabricated from one-dimensionally patterned Si and Cr. The selective emission of the emitter peaks at 3.75 µm, which targets 773K blackbody temperature, with a bandwidth of less than 1.5µm. The emission bands of this structure can also be engineered for varying source temperatures owing to the interference effects. Moreover, due to the fabrication ease, our emitter can easily be scaled up to any size of the substrate. We also present the impact of temperature and oxidation on the emission band when heated up to 1000K.

9:20am **2D+AS+BI+HC+SS-FrM-4 Advanced Two-Dimensional Nanohybrids for Efficient Electrocatalytic Hydrogen Evolution***,* ***Fei Yao,*** University at Buffalo-SUNY

Hydrogen (H_2) shows great potential in reducing greenhouse gas emissions due to its environmentally friendly nature and high gravimetric energy density. It can be generated via electrochemical water splitting based on the hydrogen evolution reaction (HER). It is well known that Pt-group metals (PGMs) are excellent catalysts for HER, but their broad adoption is limited by high cost and scarcity. Recently, two-dimensional (2D) molybdenum disulfide (MoS_2) is regarded as a promising alternative to PGMs due to its large surface area, rich active sites, and ideal hydrogen adsorption energy. However, its practical application is hindered by the intrinsically low electrical conductivity arising from the semiconducting nature of 2H phase MoS_2. On the other hand, 2D Ti_3C_2 MXene with high electrical conductivity, excellent hydrophilicity, and large interlayer distance has been intensively investigated in energy storage devices lately. Compared with charge-neutral graphene, MXene exhibits a negatively charged surface due to the existence of numerous surface functional groups (-OH, -O, -F, *etc.*), which not only enhances the dispersion of MoS_2 precursors but also promotes MoS_2 nucleation, making it a superior template for MoS_2 synthesis. Nevertheless, undesired oxidation of MXene occurs in aqueous solutions, reducing the overall catalyst stability.

To address the above issues, we employed a one-step solvothermal method using DI water/DMF as bisolvent and constructed a metallic 1T phase-enriched MoS_2/MXene/CNT composite as HER catalyst. A low overpotential (169 mV) and Tafel slope (51 mV/dec) along with the highest turnover frequency ($7\ s^{-1}$ at - 0.23V vs. RHE) and an ultralong lifetime (72 hours) was successfully achieved. The origin of the outstanding HER performance of the ternary composite can be ascribed to: (i) the prevention of 2D layer restacking as well as the enlarged surface area due to the 2D/2D MoS_2/MXene integration and ion intercalation; (ii) the vertical growth of MoS_2 flakes on the MXene template which increases the exposure of MoS_2 edge planes, maximizing the total number of active sites; (iii) the synergistically enhanced conductivity because of the formation of hybrid 1D/2D conductive network via the integration of 1T-phase metallic MoS_2, conductive MXene backbone with suppressed oxidation along with the CNT crosslinks, minimizing the charge transfer resistance at the electrode/electrolyte interface. This work demonstrated an effective strategy for two-dimensional material structure-property engineering with the aim of optimizing the HER performance which will shed light on the development of the next-generation PGM-free HER electrocatalysts.

9:40am **2D+AS+BI+HC+SS-FrM-5 Bandstructure Engineering in Two-Dimensional Semiconductors***,* ***Keun Su Kim,*** Yonsei University, Republic of Korea **INVITED**

The tunable band structure of two-dimensional quantum mater is not only interesting in itself, but also useful for the fundamental study of condensed matter physics. As example, surface chemical doping can be used to reduce the band gap of black phosphorus over the energy range greater than its intrinsic band gap [1]. This could be used to deliberately induce a topological phase transition to a Dirac semimetal phase protected by spacetime inversion symmetry [2]. It could also be used to trace the evolution of quantum phases (pseudospin) order across the topological phase transition [3]. In this talk, I will introduce our recent study on the band renormalizations and pseudogap of black phosphorus doped by alkali metals [4]. Using angle-resolved photoemission spectroscopy (ARPES), we found that the simple quadratic band dispersion of doped black phosphorus anomalously bends back towards zero wavenumber, which can be explained by Anderson-McMillan's framework developed for the band structure of liquid (or disordered) metals in the 1960s. This is a natural consequence of resonance scattering by the potential of dopant ions with short-range order. The depth of scattering potential tuned by different kinds of alkali metal (Na, K, Rb, and Cs) allows us to classify the pseudogap of p-wave and d-wave resonance.

1. J. Kim et al., Science 349, 723 (2015).
2. J. Kim et al., Phys. Rev. Lett. 119, 226801 (2017).
3. S. W. Jung, S. H. Ryu et al., Nature Mater. 19, 277 (2020).
4. S. H. Ryu, M. Huh, D. Y. Park et al., Nature 596, 68 (2021).

10:20am **2D+AS+BI+HC+SS-FrM-7 Graphene – Ferritin Interface Unpins Fermi-Level and Induces Temperature Dependent Coherent Tunneling Across Biomolecular Junctions***, **Ayelet Vilan,*** Weizmann Institute of Science, Israel*; N. Kumar Gupta,* National University of Singapore*; S. Kumar Karuppannan,* National Quantum Fabless Foundry, Singapore*; R. Reddy Pasula,* Nanyang Technological University Singapore*; J. Martin, W. Xu,* National University of Singapore*; E. May,* Nanyang Technological University, Singapore*; A. Pike,* Newcastle University, UK*; H. Astier, T. Salim,* National University of Singapore*; S. Lim,* Nanyang Technological University, Singapore*; C. Nijhuis,* University of Twente, Netherlands

Molecular electronics is one road to ultimate miniaturization: can we reduce the size of an electronic element to a size of a single molecule? However, as the size reduces to few-atoms level, it becomes harder to distinguish the role of the molecular core from that of the contacts. Here we show the prominent role of graphene interfaces with Fe storing proteins in the net charge transport across their tunnel junctions. Here, ferritin (AfFtn-AA) is adsorbed on graphene by non-covalent amine-graphene interactions. In contrast to junctions with metal electrodes, graphene has a vanishing density of states toward its intrinsic Fermi-level (“Dirac point”), which increase away from the Fermi-level. Therefore, the amount of charge carriers is highly sensitive to temperature and electrostatic charging (induced doping), as deduced from a detailed analysis of charge transport as a function of temperature. Moreover, increasing the iron loading of ferritin, changes the graphene from n- to p-doping. Remarkably, the temperature dependence can be fully explained within the coherent tunneling regime due to excitation of hot carriers. The sensitivity of graphene (and 2D materials in general) to electrostatic charging opens rich possibilities in employing interface electrostatics in tuning the electronic properties of molecular junctions and is important for 2D / biomolecules hybrids in general.

10:40am **2D+AS+BI+HC+SS-FrM-8 The Influence of Selenium Incorporation on the HER Catalytic Activity of Electrodeposited Se-MoS$_x$ Electrocatalysts***, **Lee Kendall,** G. Zangari , S. Mc,* University of Virginia

With the increase in the global consumption of energy, the need to meet the growing energy demands has put significant pressure on the current means of energy production and storage.To meet this demand, water splitting has seen substantial efforts in developing catalytically active materials that replace costly materials, such as Pt, to allow for economically viable implementations.MoS$_2$ has attracted significant attention over the past decade due to its low cost and availability. Additionally, MoS$_2$ is one of the most promising materials for electrocatalytic hydrogen evolution as its Gibbs free energy of hydrogen adsorption, $\Delta G^{H}_{0,ads-}$, is the closest to Pt, a state-of-the-art catalyst, when compared to other metallic materials. However, due to the limited number of accessible edge sites, as well as high kinetic barriers for H_2 evolution, the catalytic performance of MoS$_2$ is still far from the needed requirements. To address this, researchers have investigated amorphous MoS$_x$ due to its increased structural heterogeneity that increases catalytic site density. Combined with short-range atomic arrangements that enable adequate electronic conductivity, amorphous MoS$_x$ is an attractive candidate for electrochemical processes.This can be further improved, however, as the bridging bonds are the most catalytically active while the terminal and apical are significantly less active.To increase their activity, we investigated incorporating selenium into MoS$_x$ due to the success in crystalline, selenium alloyed MoS$_2$. This success centered on obtaining a more thermoneutral ΔG^{H}_{ads} for the sulfur edges and basal plane, similar motif to terminal and apical bonds in the amorphous system, respectively.To accomplish this, we used an electrodeposition technique that allows for the incorporation of selenium into the MoS$_x$ polymeric chains. We will report on this investigation of the electrodeposition of Se-MoS$_x$ and its effect on the physical, electronic, and catalytic properties towards the hydrogen evolution reaction. Through electrodepositing catalytically active Se-MoS$_x$ thin films, this effort demonstrates improved HER efficiency over current, low-cost materials.

11:00am **2D+AS+BI+HC+SS-FrM-9 Two-Dimensional Skintronics***, **Dmitry Kireev,** D. Akinwande,* The University of Texas at Austin **INVITED**

Modern healthcare displays a significant shift from hospital-based medicine towards a personalized, ambulatory, and wearable approach. In this regard, the development of skin-wearable electronics (*skintronics*) is an essential step toward mobile health monitoring, the healthcare Internet of Things, and eventually preventive medicine. Continuous long-term monitoring of brain activity, heart activity, body hydration, or temperature, is vital for better comprehension of human physiology, understanding systematic disease risk factors, and building preventative care solutions. In this work, we utilize *graphene* and other *2D materials* such as platinum diselenide (PtSe$_2$) and platinum ditelluride (PtTe$_2$) to construct the thinnest elements of skintronics - electronic tattoos. The PtSe$_2$ and PtTe$_2$ e-tattoos that can be grown at comparably low temperatures (400ºC) were found to have superior sheet resistance and electrode-skin impedance compared to monolayer graphene e-tattoos. On the other hand, we also report on the significant advancement of the classic graphene electronic tattoos by introducing graphene nanoscrolls and stacking multiple graphene monolayers. Moreover, we show that graphene tattoos can be made insusceptible to sweat by introducing microholes into their structure. Significantly, we show that graphene electronics tattoos can be used for deep tissue monitoring, detecting complex analytes such as blood pressure and respiration rate in a continuous and entirely non-invasive manner. Beyond the simple use of graphene tattoos as passive electronic elements, we have discovered that the semimetallic 2D material can be used as transistors, biased electrostatically through the body itself, creating transistor tattoos. The body-gated graphene tattoo transistors can function as biosensors or small-signal amplifiers, contributing to the development of higher-fidelity electrophysiology measurements and decreased susceptibility to movement-related artifacts.

11:40am **2D+AS+BI+HC+SS-FrM-11 Ultrasonic-Assisted Assembly of Metal Nanoparticles within Graphene Oxide for Tailoring Stem Cell Response***, J. Jaiswal ,* Indian Institute of Technology (Banaras Hindu University) , India*; **Marshal Dhayal,*** Indian Institute of Technology (Banaras Hindu University) , India

Recently 2D material-assisted stimulation for cellular functions has gained significant attention. In this paper, we will be presenting the methodology used for preparing tunable properties of 2D surfaces incorporating metal nanoparticles (NP) within graphene oxide sheets. The study will report the use of mechanical forces generated through an ultrasonication-assisted method for increased diffusion of metal ions in graphene oxide (GO). The transmission electron microscopy (TEM) analysis has been used to confirm the distribution of metal particles in GO sheets whereas Raman spectra were used to identify the relative changes in the Raman bands. The study presents a correlation of these observations with corresponding confirmation in the distortion of multilayer assembly of thin layers of GO by the nucleation of metal nanoparticles. The X-ray diffraction (XRD) spectra of GO-NP also demonstrated similar outcomes in Raman spectra. UV-visible spectra and X-ray photoelectron spectroscopy (XPS) analysis were used to determine optical activity and relatively % proportions of their atomic concentrations. These unique combinations of functionally graded GO-NP were used to study the response of human mesenchymal stem cells. This method may be helpful to address the challenges associated with developing metallic assembly within graphene oxide without chemical functionalization of their inert surface for their application in the biomedical field.

Surface Science Division
Room 319 - Session SS1+AS+HC-FrM

Oxide Surface Structure and Reactivity

Moderators: Andrew Gellman, Carnegie Mellon University, **Zhenrong Zhang**, Baylor University

8:20am **SS1+AS+HC-FrM-1 Operando Photoluminescence Microscopy Study of Photoreduction of Resazurin on Tio$_2$ Microcrystals***, **Hao Zhu,** Z. Zhang, W. Lu, B. Birmingham,* Baylor University

Titanium dioxide (TiO$_2$) has been extensively studied for its photo-reactivity-related applications in solar cells, clean hydrogen energy, and environmental remediation. It is commonly accepted that the anatase (A) phase is more photoreactive than the rutile (R) phase. However, the reversed relative photo activities were often reported. In addition, mixed-phase TiO$_2$ has shown the highest photoactivity but the synergetic effect is not clear. Understanding the syngenetic effect at the two-phase interface will lead to a new era of catalyst design.

In this work, operando photoluminescence microscopy was used to investigate the photoreduction of resazurin on anatase microcrystals, rutile microcrystals, rutile (110) single crystals, and anatase (001) single crystals. Our results show that the rate of resazurin photoreduction on the rutile (110) surface was higher than that on the anatase (001) surface. The reaction rates on anatase microcrystals with a large percentage (001) facet are faster than that on anatase (001) single crystals and close to the reaction rate on rutile (110) single crystals. The reaction rate of the anatase microcrystals depends on the morphology and structure of each individual particle. The mechanism of the syngenetic effects at the rutile/anatase interface was also studied on the synthesized A-R two-phase microcrystals.

8:40am **SS1+AS+HC-FrM-2 Unraveling Surface Structures of Ga-Promoted Transition Metal Catalysts in CO_2 Hydrogenation**, ***Si Woo Lee***, *M. Lopez Luna, S. Shaikhutdinov, B. Roldan Cuenya,* Fritz Haber Institute of the Max Planck Society, Germany

Gallium-containing intermetallic compounds and alloys with transition metals have recently been reported to be active in the hydrogenation of CO_2 to methanol. However, the promotional role of Ga in these catalysts is still poorly understood, in particular due to the lack of information about the *surface* structures of the catalysts, especially under reaction conditions. In this respect, studies using surface-sensitive techniques applied to well-defined model systems can provide key information to elucidate the reaction mechanism and provide the basis for the rational design of Ga-promoted TM catalysts.

In this work, we employed *in situ* Near Ambient Pressure Scanning Tunneling Microscopy (NAP-STM) and X-ray Photoelectron Spectroscopy (NAP-XPS), which make possible the studies of surfaces in the reaction atmosphere, to monitor the structural and chemical evolution of the Ga/Cu surfaces in the CO_2 hydrogenation reaction. NAP-STM images recorded in the reaction mixture revealed temperature- and pressure-dependent de-alloying of the initially formed, well-ordered c(2×2)-Ga/Cu(111) surface alloy and the formation of Ga-oxide islands embedded into the Cu(111) surface. Thus, NAP-STM studies revealed that the surface undergoes de-alloying and phase separation into Ga-oxide and (1×1)-Cu exposing Ga-oxide/Cu(111) interfacial sites. Notably, in our atomically-resolved STM image on Ga-oxide/Cu(111), it is clearly observed that Ga-oxide grows into an ultrathin oxide layer with $(4\sqrt{3}\times4\sqrt{3})R30°$ superstructure when grown on Cu(111). From NAP-XPS studies on Ga/Cu(111) in the presence of CO_2 and H_2, the formation of formate was observed, and this intermediate was finally transformed into methoxy at elevated reaction temperatures, the final surface-bound intermediate of methanol synthesis. In contrast to Ga-containing Cu catalyst, on the other hand, there was no reaction intermediate at high temperature on the Ga-free Cu(111) surface, demonstrating that the further reaction does not occur any more from chemisorbed $CO_2^{\delta-}$ on Cu alone. Therefore, the GaO_x/Cu interface formed under reaction conditions may expose catalytically active sites, that should be taken into account for elucidating the reaction mechanism on the Ga-promoted systems. For the first time, our *operando* surface characterizations reveal strong evidence that Cu–Ga catalysts are activated in CO_2 hydrogenation with the formation of embedded oxide-metal interfacial sites by de-alloying transition, which allow us to prove the promotional role of Ga in Cu-Ga catalysts.

9:00am **SS1+AS+HC-FrM-3 Stabilization of Active Cu Sites on Oxide Surfaces**, ***Dario Stacchiola,*** Brookhaven National Laboratory **INVITED**

Cu-based catalysts are active for partial and full oxidation reactions. Copper can be oxidized under moderate oxidant pressures and temperature to Cu_2O, and further to CuO under typical catalytic reaction conditions. We present here model systems using both copper oxide thin films and single crystals used to interrogate the effect of alkali, metal, and oxide modifiers on the stability of exposed active Cu sites. *In situ* experiments allow the observation of dynamic processes and phases under reaction conditions.

9:40am **SS1+AS+HC-FrM-5 An optimized IRAS Setup to Investigate Adsorbates on Metal-Oxide Single Crystals**, ***David Rath***, *J. Pavelec, U. Diebold, M. Schmid, G. Parkinson,* TU Wien, Austria

The IRAS system GRISU (**GR**azing incident **I**nfrared absorption **S**pectroscopy **U**nit) was developed to investigate adsorbates on metal oxide single crystals with maximum sensitivity. GRISU combines the commercially available FTIR spectrometer Bruker Vertex 80v with a UHV chamber [1].

The compact design utilizes only one CF150 flange (6”) on the UHV chamber, ensuring the precise positioning of all the optical components and the high-performance requirements.

The system features five mirrors for beam guidance placed in HV and UHV environments and optimizes the system's performance, flexibility, and usability. The result is a small controllable focal-spot diameter (max. 3 mm) on the sample, motorized optical components, and apertures that control the shape of the illumination area on the sample to reduce the background signal. A second aperture limits the incidence angle range of the infrared radiation illuminating the sample. Incidence angles between 49° and 85° are possible.

The simulated system (done with a ray-tracing program and a simplified spectrometer model) shows an efficiency of 13 %, i.e., 13 % of the radiation passing through the first aperture (Ø 6 mm) after the IR source in the FTIR spectrometer reaches the detector after being reflected from the molecular beam spot (Ø 3.5 mm) on the sample. Compared to a commercially available system with two parabolic mirrors with a focal length of 250 mm, the efficiency is about 20x higher.

The performance of the system is demonstrated by first measurements.

[1] J. Pavelec, et al., J. Chem. Phys. 146, 014701 (2017).

10:00am **SS1+AS+HC-FrM-6 Photochemical Fluorination of TiO_2(110)**, ***Melissa Hines***, *W. DeBenedetti, Q. Zhu, M. Hasany, D. Somaratne,* Cornell University

Fluorine has been widely reported to improve the photoreactivity of TiO_2 nanocrystals, but surface science studies of this enhancement have been stymied by the lack of well controlled fluorination chemistries. Fluorine-terminated rutile (110) surfaces were produced by the photochemical degradation of solution-prepared carboxylate monolayers in the presence of XeF_2 (g) at room temperature. The reaction initially produces a multi-nanometer-thick surface layer with a nominal composition of $TiOF_2$. The $TiOF_2$ layer largely dissolves with immersion in room temperature H_2O, leaving behind a fluorinated surface terminated by 0.8 monolayers of F bound to initially undersaturated Ti atoms. Scanning tunneling microscopy images showed that the fluorinated surface was rough on an atomic scale, displaying short, atomically straight rows parallel to the [001] direction. The fluorinated surface remained notably contamination free, even after immersion in solution and exposure to air for tens of minutes. The relatively high reactivity of the $TiOF_2$ surface layer towards etching can be rationalized in terms of disrupted charge balance in the surface layer. Consistent with this, density functional theory simulations showed that the removal of bridging O atoms from the fully fluorinated surface to produce O_2 would be exoergic.

10:20am **SS1+AS+HC-FrM-7 Surface Structures of $La_{0.8}Sr_{0.2}MnO_3$ (001) Thin Films**, ***Erik Rheinfrank***, *M. Brunthaler, G. Franceschi, M. Schmid, U. Diebold, M. Riva,* Institute of Applied Physics, TU Wien, Austria

Lanthanum-strontium manganite ($La_{0.8}Sr_{0.2}MnO_3$, LSMO) is a perovskite oxide used as a cathode material in solid oxide fuel cells, which convert chemical energy to electrical energy. To gain deeper insights into the reaction mechanisms, it is important to understand the structure of the surface at the atomic scale. To this end, we grow atomically flat single-crystalline LSMO thin films on Nb-doped $SrTiO_3$ (STO) substrates via pulsed laser deposition (PLD). Previously, this has been achieved already for the (110) orientation [1,2]. Here, we use a similar approach on the (001) surface that is commonly used for oxide-based electronics and spintronics. The as-grown films were transferred in UHV from the PLD chamber to a surface science system, and characterized with scanning tunneling microscopy, x-ray photoelectron spectroscopy, and low-energy electron diffraction. We show how the LSMO surface structures change due to variation of the oxygen chemical potential upon annealing. Moreover, Ar^+ sputtering and subsequent annealing removes preferentially Mn over La. This can be exploited to transform a B-site (Mn) terminated surface into an A-site (La/Sr) rich surface. The B-site terminated surface is recovered by depositing Mn from an MnO target.

[1] Franceschi et al., J. Mater. Chem. A, 2020, **8**, 22947-22961

[2] Franceschi et al., Phys. Rev. Materials, 2021, **5**, L092401

10:40am **SS1+AS+HC-FrM-8 Adsorption of Organophosphate Nerve Agent VX on the (101) Surface of Anatase Titanium Dioxide**, ***Gloria Bazargan***, NRC Research Associate, U.S. Naval Research Laboratory; *I. Schweigert, D. Gunlycke,* Chemistry Division, U.S. Naval Research Laboratory

We quantify the adsorption of the organophosphate venomous agent X (VX) on the clean and hydroxylated (101) surfaces of anatase titanium dioxide (TiO_2) with density functional theory (DFT) calculations. Our results show that adsorption on the clean anatase (101) surface occurs through the VX phosphoryl oxygen (O=P) site and involves the formation of a Ti⋯O=P dative bond. Steric effects inhibit adsorption through the VX nitrogen and sulfur sites by the formation of Ti⋯N and Ti⋯S dative bonds. On the hydroxylated (101) surface, adsorption similarly proceeds through the VX phosphoryl oxygen site but entails the formation of surface–adsorbate hydrogen bonds. Additionally, weak non-covalent interactions between the surface hydroxyl groups and the adsorbate’s nitrogen and sulfur atoms stabilize VX/(101) complexes formed by adsorption through these secondary sites.

Author Index

Bold page numbers indicate presenter

Author Index

Author Index