Monday Afternoon, September 22, 2025

Surface Science Room 209 CDE W - Session SS-MoA

Photo/Electrochemistry

Moderators: Liney Arnadottir, Oregon State University, Dario Stacchiola, Brookhaven National Laboratory

1:30pm SS-MoA-1 Plasmonic Catalysis: Opportunities, Challenges, and Unresolved Questions, *Suljo Linic*, University of Michigan, USA INVITED Metallic plasmonic nanostructures have emerged as an important class of optically active materials. The initial interest in these materials was based on their nano-antenna properties where these materials concentrate electromagnetic UV-vis fields in small volumes at the surface of the nanostructure. A critical problem with using these metallic materials as nano-antennas is that they lose a significant fraction of electromagnetic energy due to the formation of energetic electron-hole (e-h) pairs in the nanostructures.

There has been a growing realization that the formation of energetic charge carriers in the nanoparticles opens avenues for a number of applications including photocatalytic chemical conversion. At the core of these applications is the need to control the rate of formation of energetic e-h pairs, the location of their formation, and their flow in the nanostructure. There has been a high degree of interest in using hybrid nanostructures containing plasmonic nanoparticles, where the plasmonic component controls the interaction of light with the material, while the non-plasmonic component uses the resultant energetic carriers to perform a function. Examples of these materials include metal-metal, metal-semiconductor or metal-molecule hybrids. The use of these multicomponent materials introduces a number of fundamental questions related to the impact of the interface between the plasmonic and non-plasmonic component as well as the presence of the non-plasmonic material on the optical properties of the system, the flow of energy and excited charge carriers in the system.

I will discuss our work in the emerging field of hybrid plasmonic materials, focusing on the underlying physical principles that govern the flow of energy and excited charge carriers in these systems, as well as on common misconceptions and fundamental questions that deserve more attention and warrant additional studies.

References

- 1. Christopher, P., Xin, H., and Linic, S. *Nature Chem* **3**, 467-472 (2011).
- Boerigter, C., Aslam, U., and Linic, S. ACS Nano 10, 6, 6108-6115 (2016).
- Linic, S., Chavez, S., and Elias, R.C. Nature Mater 20, 916-924 (2021).
- 4. Chavez, S. and Linic, S. *Nano Energy* **98**, 107244 (2022).
- 5. Elias, R.C., Yan, B., and Linic, S. *JACS* **146**, 43, 29656-29663 (2024).

2:00pm SS-MoA-3 Effects of Electric Fields and Solvents on the Surface Chemistry of Catalysis and Electrocatalysis, Charles T. Campbell, University of Washington

Understanding how liquid solvents affect the adsorption energies of catalytic reaction intermediates on transition metal surfaces, compared to their better-known values in gas phase, is crucial for understanding liquidphase catalysis and electrocatalysis. For neutral adsorbates, the dominant effect is a decrease in adsorption energy compared to the gas phase by an amount equal to the solvents' adhesion energy to the solid multiplied by the surface area of the solid (that is blocked from solvent adsorption) per mole of adsorbed reactant. However, the electric field near the surface also has a strong effect on adsorption energies. When thermal catalytic or electrocatalytic reactions occur on metal surfaces in liquid solvents like water, an electrical double layer develops near the metal surface with a large electric field which changes with reaction conditions. This electric field affects the energies of adsorbed reaction intermediates and transition states, and therefore reaction rates. I will review ultrahigh vacuum (UHV) surface science studies regarding the effects of electric fields on the energies of adsorbed catalytic reaction intermediates, and show how these can guide predictions about how changes in electric fields from the double layer affect adsorbate energies on metal surfaces in liquids, and serve as benchmarks for validating accuracy of computational studies. In UHV, the

electric field felt by an adsorbate can be strongly tuned by the addition of another adsorbed species nearby. Alkali adatoms exert a very strong change in electric field near the metal surface, which changes the energies of coadsorbed catalytic reaction intermediates, their electronic character and their reaction rates, as has been studied extensively in UHV. Assuming that changes in the field have only small effects on the strength of the weak attractions between adsorbate and solvent, the change in adsorbate energy with local electric field in a liquid is the same as in UHV. This approach explains the well-known observation that the binding energy of hydrogen adatoms (H_{ad}) to many late transition metal surfaces, as probed by cyclic voltammetry in water, increases with increasing pH. This change in H_{ad} energy in turn explains pH-induced changes in thermal catalytic and electrocatalytic hydrogenation reaction rates whereby H_{ad} must add to another species.

2:15pm SS-MoA-4 In Air STM Observation of Au(111) Surface Disturbance Including Au Magic Fingers as Modified by Solvent Choice, Nazila Hamidi, Erin Iski, Dillon Dodge, Rowan Dirks, Lauren Hornbrook, University of Tulsa The formation of Au magic fingers on Au(111) surfaces, a phenomenon first observed under "pristine" ultra-high vacuum (UHV) conditions, has long fascinated researchers due to its implications for nanoscale surface manipulation and quantum effects. This study explores the formation of these structures under more relevant conditions, specifically in air and at room temperature, using Scanning Tunneling Microscopy (STM). After exposing Au(111) to a 0.1 M solvent solution, three types of surface disturbances were observed, including the formation of Au magic fingers. The disturbance mechanism involved strong tip-surface interactions and the mass transport of Au atoms, influenced by the solvent choice. Various solvents, including HClO₄, HNO₃, HCl, NaOH, CH₂O₂, CHCl₃, C₅H₅N, and $C_2H_4O_2$, were tested for their effects on the surface disturbances. The degree of disturbance was categorized into significant & organized disturbance (SOD), significant & disorganized disturbance (SDD), and insignificant disturbance (IND).

The formation of Au magic fingers was primarily observed with solvents classified under SOD, such as HClO₄ and HNO₃, which facilitated the diffusion of Au atoms at a rate of 9.9 ± 1.1 nm²/min. Solvents in the SDD category, like CH_2O_2 , showed a diffusion rate of 4.0 ± 1.9 nm²/min. Our findings reveal that the chemical properties of the solvent, particularly its total charge and electronegativity, play a pivotal role in modulating the surface dynamics of Au(111). The mechanism for the formation of Au magic fingers likely involved the adsorption of solvent molecules to the STM tip, which then picked up and moved Au atoms from the step edges to form nanowires. This study advances our understanding of solvent-surface interactions and demonstrates the potential for ambient STM to probe and manipulate nanostructures under practical, real-world conditions. The ability to form organized nanostructures like Au magic fingers in the air, without needing UHV or protective liquid layers opens new avenues for nanotechnology, catalysis, and surface chemistry applications. By bridging the gap between fundamental surface science and applied chemistry, this work underscores the importance of solvent choice in controlling nanoscale phenomena and paves the way for future innovations in nanomaterial design.

2:30pm SS-MoA-5 Size-Selected Pt Clusters on N-Implanted HOPG: Oxygen Reduction Reaction and the Effect of Nitrogen Anchor Sites, Lokesh Saravanan, University of Utah; Tsugunosuke Masubuchi, Keio University, Japan; Zihan Wang, University of Utah; Pavel Rublev, Yu Wei, Anastassia N Alexandrova, University of California at Los Angeles; Scott L Anderson, University of Utah

Platinum clusters (Ptn) have been considered as an effective electrocatalyst for the oxygen reduction reaction (ORR), the hydrogen evolution reaction and alcohol oxidation. In this work, atomically size-selected Pt₂ were deposited under soft landing conditions (≤2 eV/atom) on indium tin oxide (ITO) and highly-oriented pyrolytic graphite (HOPG) electrodes in ultra-high vacuum, then studied electrochemically. The ORR activity exhibited strong substrate dependence, with Ptn on HOPG showing up to a ~5 times increase in mass activity compared to Ptn on ITO. However, clusters on pristine HOPG are unstable due to sintering, dissolution, and surface poisoning. To overcome the stability issue, nitrogen implantation has been employed to create anchoring sites on HOPG (N-HOPG). Pt_n deposited on N-HOPG showed improved stability against sintering and dissolution while retaining their high catalytic activity. The catalysts have been characterized by a combination of scanning tunneling microscopy (STM) and scanning transmission electron microscopy. X-ray photoelectron spectroscopy (XPS) provided direct evidence of Pt-N interactions, revealing the nitrogen

Monday Afternoon, September 22, 2025

species that serve as chemically active binding sites. Density functional theory (DFT) calculations were performed to simulate both the clustersurface interaction and the impact dynamics of N/N₂ ions during implantation. These simulations suggests that ion bombardment leads to penetration and modification of surface graphite layers, promoting the formation of anchor or defect-rich sites favorable for Pt_n stabilization. These findings can provide fundamental insights into cluster stabilization mechanisms and the role of nitrogen anchoring sites on HOPG, offering a broader understanding of electrochemical transformations involving various metal clusters. I would like to acknowledge the support from the U.S. Department of Energy, Office of Science, under grant number DE-SC0020125.

2:45pm SS-MoA-6 Promoting Electrochemical Reactions Using Like-Charged Co-Ions, *Matthew Gebbie*, University of Wisconsin - Madison

The rates and selectivity of electrochemical reactions often hinge on processes occurring at charged electrode-electrolyte interfaces, where molecular forces cause electrolyte ions to be attracted to or repelled from interfacial environments. Generally, oppositely charged counterions are attracted and like-charged co-ions are repelled from interfaces, leading to charge separation that screens surfaces. Yet, this ion de-mixing also incurs substantial entropic penalties. Electric double layer formation describes how electrostatic and entropic forces balance to govern ion distributions and charge transfer at interfaces. While classical models for double layer formation predict co-ions are excluded from charged surfaces, I will discuss our discovery that co-ions can play a defining role in electrocatalytic reactions under the high surface potentials that are inherent to many electrochemical systems, even under low ion concentrations where the bulk electrolyte is expected to behave classically. I will highlight our investigation using in situ analysis of ion surface assembly during the hydrogen evolution reaction to reveal how co-ion properties can influence reactivity to a greater degree than counterion properties, contradicting expectations from classical theory. I will also discuss how our findings generalize to CO2 reduction, where we demonstrate that co-ions also play a defining role in ionic liquid-mediated CO₂ conversion to CO. More broadly, we reveal that co-ions can be designed with chemical functions, such as being a hydroxide sink to dynamically "buffer" interfaces, to promote electrocatalytic conversion of water, CO2, and other surface reactions critical to energy storage and conversion.

3:00pm SS-MoA-7 X-Ray Photoelectron Spectroscopy informs on Hybrid Photoelectrode Surface Passivation and Durability, Jillian Dempsey, University of North Carolina at Chapel Hill INVITED

Integration of CO₂ reduction molecular catalysts with silicon photoelectrodes can be achieved through covalent attachment methods, such as hydrosilylation, where hydrogen-terminated silicon is reacted to form silicon-carbon bonds. These hybrid photoelectrodes use sunlight to drive the conversion of CO₂ to value added fuels and chemicals. Incomplete reaction of the atop silicon sites can leave reactive sites that are prone to corrosion and lead to the formation of defects that trap photogenerated carriers. X-ray photoelectron spectroscopy provides critical information both on the success of the catalyst attachment, as well as the extent of passivation through detection of SiO₂ growth. Further, XP spectra recorded before and after controlled potential photoelectrolysis inform on the durability of the covalently modified silicon surface and guide the development of improved hybrid photoelectrodes.

3:30pm SS-MoA-9 Surface Analysis of Planetary Regolith Particles: X-Ray Photoelectron Spectroscopy Results from the Asteroid Bennu, Catherine Dukes, Lianis Reyes Rosa, Adam Woodson, Jackson Glass, Annabel Li, University of Virginia; Christopher Snead, Lindsay Keller, NASA Johnson Space Center; Michelle Thompson, Purdue University; Harold Connelly, Jr., Rowen University; Dante Lauretta, University of Arizona; OSIRIS-REx Sample Analysis Team, NASA

NASA's OSIRIS-REx mission to near-Earth primitive asteroid Bennu returned >120 grams of regolith. The rims of planetary regolith particles can exhibit a composition that is significantly different from the bulk, due either to geochemical processes on the parent body—such as interactions with aqueous environments—or to space weathering processes, including meteoritic impacts or solar wind irradiation. We investigate the surface composition of multiple Bennu particles from aggregate sample OREX-803205-0 via X-ray photoelectron spectroscopy (XPS). We compare these values with published bulk elemental abundances as well as energy-dispersive X-ray (EDS) spectroscopic measurements. XPS analyses were performed on a PHI Versaprobe III small spot instrument; SEM/EDS

measurements were made with an FEI Quanta 650 with Oxford silicon drift detector.

The near-surface compositions of the >1 mm particles we analyzed are relatively homogeneous and comparable to the bulk elemental content [1], containing Mg, Si, O, Na, Fe, S, Al, Cr, Mn, C, Cl, and F [2]. The Bennu particle surfaces exhibit lower carbon and oxygen signatures (C: 11–13.4 at-%, O: 56–60 at-%) than the Murchison meteorite surfacial concentrations (C: 16–19 at-%, O: 60–64 at-%) — presumably the result of controlled sample handling and/or indicative of space weathering [3]. The surface abundances of Na (0.6–2.8 at-%), Mg (10.1–13.4 at-%), and Si (10.1–11.9 at-%) are significantly greater for Bennu than Murchison, where <<1 at-% Na has been observed and Mg content is only 3–5 at-% [3]. No Ca was observed on the Bennu particle rims, which is surprising because ICP-MS bulk analysis identifies Ca at concentrations similar to Na [1]. These differences may be the result of sample inhomogeneities, but are most probably indicators of aqueous exposure.

The <1 mm Bennu regolith particles that we analyzed have surface constituents identical to those of the >1 mm particles but exhibit more compositional variation. In particular, S (to 2.1%) and Na (to 3.8%) are highly enriched on some particles. Na enrichment may have originated from salty precipitates generated by a subsurface brine within Bennu's parent body [4], such exposure can also preferentially leach elements such as calcium from particle rims [5].

Acknowledgments: This material is based upon work supported by under contract no. NNM10AA11C issued through the New Frontiers Program.

References: [1] Lauretta & Connolly et al (2024) Meteorit Planet Sci 59, 2453–2486 [2] Dukes et al (2025) 56th LPSC, Abst#2322 [3] Laczniak et al (2021) Icarus 364, 114479 [4] McCoy & Russell et al (2025) Nature 637, 1072–1077 [5] Cantando et al (2008) J Geophys Res 113, E09011.

4:00pm SS-MoA-11 Investigation of the Interaction between Water Vapor and Ni Nanoparticles Supported Over Ceria, Nishan Paudyal, Erik Peterson, Yinghui Zhou, University of Wyoming; Sanjaya Senanayake, Brookhaven National Laboratory; Jing Zhou, University of Wyoming

Understanding the role of water vapor in the growth and sintering of ceriasupported Ni nanoparticles is important since it can provide insights into their promising activity towards reactions in which water is a key reactant. In our study, we prepared fully oxidized CeO₂(111) and partially reduced CeO1.75(111) thin films as model catalytic supports for Ni and studied the detailed nucleation, size, and distribution of Ni nanoparticles under ultrahigh vacuum (UHV) conditions using scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS). Deposition of Ni with submonolayer coverages at 300 K produces small particles that are uniformly distributed over both oxidized and reduced ceria surfaces. The particles agglomerate into large three-dimensional features that are on average 1.0 nm high after heating to 700 K. Furthermore, the particles show a clear preferential decoration at step edges on CeO₂ due to enhanced diffusion at elevated temperatures. The Ni particle growth with heating was also observed over reduced ceria. However, due to a stronger interaction between Ni and reduced ceria with defects (e.g. oxygen vacancies/Ce3+), smaller Ni particles are formed over CeO1.75. Exposure of water vapor to the Ni/ceria surface at 300 K can influence the sintering behavior of Ni, causing the formation of significantly flatter particles with heating compared to Ni over adsorbate-free ceria that are attributed to unique adsorbate-metal-oxide interactions. We also conducted the experiments when water was first dosed onto ceria supports followed by subsequent Ni deposition at 300 K. Surface defects (e.g. oxygen vacancies) over reduced ceria are the active sites for water dissociation to form hydroxyl groups at 300 K. This creates fewer nucleation sites for Ni upon deposition over CeO_{1.75} at room temperatures and an extensive decrease in its particle density. Predosed water over CeO1.75 also causes significant sintering of Ni nanoparticles with subsequent heating to higher temperatures. Our experimental findings suggest distinct adsorbate-metaloxide interactions are key to tune the properties of Ni nanoparticles over reducible CeO_x(111) surfaces caused by water exposure. Such interactions are essential in consideration for further modification of Ni-based catalysts for improved reactivity and stability.

Monday Afternoon, September 22, 2025

4:15pm SS-MoA-12 The Effect of Surface Reaction Intermediates on the Interaction of Solvent Molecules with Pt(111) Model Catalyst, Valeria Chesnyak, Oregon State University; Arjan Saha, Washington State University; Marcus Sharp, University of Washington; Zbynek Novotny, Pacific Northwest National Laboratory; Nida Janulaitis, Charles T. Campbell, University of Washington; Zdenek Dohnalek, Pacific Northwest National Laboratory; Liney Arnadottir, Oregon State University

The interaction energies of molecules with solvents on metal surfaces contribute to processes in heterogeneous catalysis and electrocatalysis. Such interactions are essential in catalytic biomass conversion reactions, pollution cleanup, and energy transition. The impact of solvents on the adsorption energetics of reactants, reaction intermediates, and transition states determines reaction rates and selectivity. While adsorption enthalpies of many reactants on metal surfaces in vacuum have been reported, how they change in the presence of liquids remains poorly understood.¹ Computational methods such as density functional theory (DFT) can predict adsorption energies, including coadsorption and solvation effects at the reactant-solvent-catalyst interface. However, these models require experimental benchmarks for validation, as significant discrepancies persist between calculated and experimental adsorption enthalpies. We present here results aimed to provide such benchmarks for the interaction energies between adsorbed intermediates and solvents on metal surfaces.

Single Crystal Adsorption Calorimetry (SCAC) is the only technique capable of directly measuring the molecular and dissociative enthalpies of adsorption on well-ordered single crystalline surfaces. We employ a state-of-the-art microcalorimeter, developed by the Campbell group,² to understand coadsorption-induced effects of common agents in catalysis on surfaces. Specifically, we measure the differential heats of adsorption for water and methanol coadsorbed with CO or hydrogen on clean Pt(111). On Pt(111), CO forms a $\sqrt{3} \times \sqrt{3}$ R30° structure, while molecular hydrogen dissociates to form a (1×1) hydrogen atom adlayer at cryogenic temperatures (100 K). Understanding the effects of these pre-adsorbed catalytic intermediates on the adsorption energies of the solvents provides important benchmarks for validating computational models.

References:

¹ Bligaard, T., et al. "Toward benchmarking in catalysis science: best practices, challenges, and opportunities." **2016** ACS Catalysis 6(4), 2590-2602.

² Ajo, Henry M., et al. "Calorimeter for adsorption energies of larger molecules on single crystal surfaces." **2004** *Review of Scientific Instruments* 75(11) 4471-4480.

4:30pm SS-MoA-13 Understanding Interfacial Structure to Enhance Electrochemical Capacitance in Ionic Liquid Electrolytes, Hrishikesh Tupkar, Sila Alemdar, Jack Verich, Jack McAlpine, Matthew Gebbie, University of Wisconsin-Madison

Growing use of intermittent wind and solar energy necessitates research into new materials and devices that can compensate grid-scale power fluctuations. This creates a new role for high power density supercapacitors that quickly charge and discharge excess electrochemical energy. An ideal supercapacitor electrolyte has a wide electrochemical stability window and high capacitance to maximize energy density. Ionic liquids (ILs) show potential as supercapacitor electrolytes with their wide electrochemical stability windows, nonflammability, and nonvolatility. Yet, pronounced ionion correlations present in ILs often result in low capacitances, particularly at large voltages. I will discuss our work aimed at tuning ionic correlations in IL blends to provide pathways towards higher energy density capacitive interfaces. We find that mixing surface-active amphiphilic anions into ILs doubles the capacitance at negative surfaces. Therefore, we hypothesize that anion-anion van der Waals interactions weaken IL cation-anion interactions and drive molecular assembly at negative surfaces, increasing capacitance. We also observe that co-ions, or ions of same charge to the surface, play an equivalent role to counterions, ions of opposing charge to the surface, at dictating interfacial capacitance in IL mixtures. We then investigate the interfacial structure of ionic liquid mixtures using surface forces measurements to understand the mechanism behind increased capacitances. Ultimately, these investigations inform the role of co-ions and mixture entropy at promoting self-assembly to design higher energy density ionic liquid electrolytes for supercapacitors.

4:45pm SS-MoA-14 Studying the Intermolecular Forces That Drive Magic Number Clustering, Alex Walter, S. Alex Kandel, University of Notre Dame The intermolecular forces that drive crystallization also drive cluster formation in solution. These clusters can be measured using electrospray ionization mass spectrometry (ESI-MS) as the soft ionization technique does not break up supramolecular clustering, and the information can be used to study pathways to bulk crystallization. Clusters that appear at higher frequencies than would be expected are called magic number clusters and have highly favorable geometries, charge distributions, or energies. In a solution together, guanine and cytosine form magic number tetramers (3:1 guanine: cytosine). During MS/MS experiments, the tetramers break into guanine dimers and 1:1 guanine: cytosine clusters. This is not the expected Watson-Crick binding pattern, but rather a Hoogsteen binding pattern where the N7 purine and the C4 amino group are binding to the N3 and C4 positions of the other guanine. Replacing a guanine with a cytosine stretches this geometry. Substituting the guanines with 9-methylguanine shows the same binding pattern, as the N9 position does not participate in the Hoogsteen binding, but replacing the guanines with 6-O-methylguanine breaks this clustering entirely as the methyl group sterically blocks magic number cluster formation. This technique is applied to other systems, including melamine with cvanuric acid and adenine with thymine/uracil to learn more about magic number clustering, the intermolecular forces that drive solution assembly, and crystallization.

Author Index

-A-Alemdar, Sila: SS-MoA-13, 3 Alexandrova, Anastassia N: SS-MoA-5, 1 Anderson, Scott L: SS-MoA-5, 1 Arnadottir, Liney: SS-MoA-12, 3 -c-Campbell, Charles T.: SS-MoA-12, 3; SS-MoA-3, **1** Chesnyak, Valeria: SS-MoA-12, 3 Connelly, Jr., Harold: SS-MoA-9, 2 _D_ Dempsey, Jillian: SS-MoA-7, 2 Dirks, Rowan: SS-MoA-4, 1 Dodge, Dillon: SS-MoA-4, 1 Dohnalek, Zdenek: SS-MoA-12, 3 Dukes, Catherine: SS-MoA-9, 2 — G — Gebbie, Matthew: SS-MoA-13, 3; SS-MoA-6, 2 Glass, Jackson: SS-MoA-9, 2 -H-Hamidi, Nazila: SS-MoA-4, 1

Bold page numbers indicate presenter Hornbrook, Lauren: SS-MoA-4, 1 -1-Iski, Erin: SS-MoA-4, 1 _J_ Janulaitis, Nida: SS-MoA-12, 3 —к— Kandel, S. Alex: SS-MoA-14, 3 Keller, Lindsay: SS-MoA-9, 2 -L-Lauretta, Dante: SS-MoA-9, 2 Li, Annabel: SS-MoA-9, 2 Linic, Suljo: SS-MoA-1, 1 -M-Masubuchi, Tsugunosuke: SS-MoA-5, 1 McAlpine, Jack: SS-MoA-13, 3 — N -Novotny, Zbynek: SS-MoA-12, 3 -P-Paudyal, Nishan: SS-MoA-11, 2 Peterson, Erik: SS-MoA-11, 2 — R — Reyes Rosa, Lianis: SS-MoA-9, 2

Rublev, Pavel: SS-MoA-5, 1 -s-Saha, Arjan: SS-MoA-12, 3 Sample Analysis Team, OSIRIS-REx: SS-MoA-9, 2 Saravanan, Lokesh: SS-MoA-5, 1 Senanayake, Sanjaya: SS-MoA-11, 2 Sharp, Marcus: SS-MoA-12, 3 Snead, Christopher: SS-MoA-9, 2 —т— Thompson, Michelle: SS-MoA-9, 2 Tupkar, Hrishikesh: SS-MoA-13, 3 -v-Verich, Jack: SS-MoA-13, 3 -w-Walter, Alex: SS-MoA-14, 3 Wang, Zihan: SS-MoA-5, 1 Wei, Yu: SS-MoA-5, 1 Woodson, Adam: SS-MoA-9, 2 —z— Zhou, Jing: SS-MoA-11, 2 Zhou, Yinghui: SS-MoA-11, 2