

## Advanced Microscopy and Spectroscopy to Explore Field-Assisted Chemistry

Room 116 - Session AMS2-WeA

## Advanced Microscopy and Spectroscopy to Explore Field-Assisted Chemistry II

**Moderators:** **Sten Lamberts**, Pacific Northwest National Laboratory, **Daniel E Perea**, Pacific Northwest National Laboratory

4:15pm **AMS2-WeA-9 Lanthanide Adsorption in Micas: The Implications for Rare Earth Elements Separations**, *Y. Wen*, US DOE Ames National Laboratory; *K. Verma*, Ames National Laboratory; *D. Jing*, Iowa State University; *M. Lacount*, *S. Kathmann*, Pacific Northwest National Laboratory; *Tanya Prozorov*, US DOE Ames Laboratory

**INVITED**

Rare earth elements (REEs) are critical to the economic growth and national security of the United States, but their supply chain is vulnerable to disruptions. To harness underutilized sources of REEs, it is important to understand the localized environments in which these elements occur. Regolith-hosted ion-adsorption clays selectively absorb heavy REEs (HREEs) released through the weathering and dissolution of granites and other igneous rocks by rainwater. This REE adsorption trend is recognized, yet the adsorption mechanisms remain poorly understood.

Our results show that micas, which are structurally and chemically similar phyllosilicates, exhibit a different pattern of REE adsorption. Notably, micas adsorb Nd (a light REE) more readily than Yb (a heavy REE), deviating from the HREE adsorption trend in regolith-hosted clays. Our findings further revealed the colocalization of lanthanides with impurity ions within the mica structures, underscoring the significant role of internal electric potentials in influencing REE adsorption. This unusual adsorption behavior in micas due to the electric potentials within their structure provides crucial experimental evidence that impurities can be used to tune REE adsorption and separation in layered materials.

We employ scanning transmission electron microscopy in combination with analytical spectroscopy and electron holography experiments for detailed spatio-chemical analysis of micas exposed to aqueous solutions containing Nd and Yb. We monitor the d-spacing of minerals, using it as a single electron beam-damage indicator throughout our imaging and spectral analysis processes. Atom Probe Tomography (ATP), X-ray Photoelectron Spectroscopy (XPS) and computational modeling in combination to deepen our understanding of the fundamental factors that govern REE adsorption in micas. These insights are instrumental in guiding the development of novel geo-inspired materials for the effective separation of rare earth elements from diverse feedstocks.

4:45pm **AMS2-WeA-11 Single-Molecule Spectroscopic Probing of N-Heterocyclic Carbenes on a Two-Dimensional Metal**, *Nan Jiang*, University of Illinois Chicago

N-heterocyclic carbenes (NHCs) have recently proven to be powerful ligands for planar surface modification due to their remarkable structural diversity, property tunability, and high affinity to a diverse array of elements. However, the utilization of NHCs for planar surface modification has almost exclusively been limited to bulk substrates; the exploration of NHC modification of two-dimensional (2D) materials remains largely uncharted despite its promise for wide energy and electronic applications. Here we investigate the adsorption of NHCs on a 2D metal, specifically monolayer boron (i.e., borophene), at the single-molecule level using tip-enhanced Raman spectroscopy, scanning tunneling microscopy/spectroscopy (STM/S), and density functional theory calculations. Single-molecule optical spectroscopy reveals the distinct interfacial interactions between individual NHCs and borophene, in covalent (boron-carbon bonding) and van der Waals-type manners, highlighting the role of steric effects in determining the binding mode. Furthermore, the impact of NHC adsorption on borophene's electronic properties is demonstrated by local work function reductions, as measured quantitatively by single-molecule STS. In addition to providing novel insight into NHC-substrate interactions in the 2D regime, this study opens up an avenue for single-molecule studies of NHC chemistry, promising to promote advances in understanding and inform ongoing efforts to devise and realize new NHC-related applications.

5:00pm **AMS2-WeA-12 Electric Fields and CO<sub>2</sub> Coverage Effects on the Surface Chemistry of La-Based Perovskites**, *Ariel Whitten*, *J. McEwen*, Washington State University; *E. Nikolla*, University of Michigan, Ann Arbor; *R. Denecke*, Leipzig University, Germany

Perovskite-based materials are more stable than metal anode catalysts in electrochemical CO<sub>2</sub> reduction processes, but perovskites have reduced activity as compared to metal catalysts such as Ni. For perovskites to be an alternative catalyst for this process, the perovskite surface needs additional augmentations to increase the activity such as the introduction of active sites like oxygen vacancies or external influences like electric fields. We propose using La-based perovskites (LaNiO<sub>3</sub>, LaCoO<sub>3</sub> and LaFeO<sub>3</sub>) which are known to be highly active in CO<sub>2</sub> reduction and investigate these surfaces using both experimental and first principles-based calculations. In a previous project, we deconvoluted XPS spectra of LaNiO<sub>3</sub> and LaCoO<sub>3</sub> finding that the higher energy peak in the O 1-s spectra occurred in large part to the adsorption of water but other adspecies (H, O, OH and CO<sub>2</sub>) gave smaller contributions to the peak. Although understanding the surface science of co-electrolysis with H<sub>2</sub>O and CO<sub>2</sub> is the ultimate goal of the project, the adsorption and conversion of CO<sub>2</sub> are a widely acknowledged barrier to CO<sub>2</sub> reduction. Therefore, studying the nature of CO<sub>2</sub> interactions with the surface is imperative to building on the critical knowledge needed to improve this process. From our initial results studying CO<sub>2</sub> adsorption at differing coverages (Figure 1), we find that interactions calculated using the lattice gas method between adspecies travel mainly through the surface (Figure 2) and cause a surface rearrangement depending on adsorbate configuration, adsorption strength and B-site material. This indicates the limiting factor of CO<sub>2</sub> adsorption is the concentration of charge in the surface that is necessary to stabilize the adspecies. The stabilization of adsorbates can therefore be improved by adding charge via external electric fields. Our studies of electric fields on clean surfaces indicate that increased electric fields lead to a drastic fluctuation in the plane averaged local potential, which can decrease the stability of the surface. Thus, the strength of the electric field needs to be calibrated so that it adds charge to the surface without causing its decomposition. Moreover, the formation of surface oxygen vacancies is spontaneous under negative electric fields on LaFeO<sub>3</sub>. Thus, the perovskite anode of an electrochemical cell will form active sites that spontaneously increase its activity. In further studies, we aim to understand the effects of coverage on the adsorption of CO<sub>2</sub> using nudged elastic band calculations and an effect of electric fields has on the adsorption and activation of CO<sub>2</sub>.

5:15pm **AMS2-WeA-13 Interfacial Quantum Electric Fields**, *Shawn Kathmann*, Pacific Northwest National Laboratory

Electric fields and voltages within and at the interfaces of matter are relevant to catalysis, crystallization, materials science, biology, and aqueous chemistry. Accurate measurements of fields and voltages of matter has been achieved using electron holography/tomography (EHT) and can be directly compared with quantum mechanical calculations. From these findings all interfaces have large intrinsic local electric fields ( $\sim 10$  GV/m =  $1$  V/Å) and voltages even if these materials are macroscopically electrically neutral. The use of very weak applied fields ( $<10^{-3}$  V/Å) causes materials to respond, changing both the magnitude and spatial distribution of the intrinsic electric fields. The resulting interfacial response fields, i.e.,  $E_{\text{resp}}(r) = E_{\text{intr}}(r) + E_{\text{appl}}(r)$ , have been measured using EHT and are similarly large as the intrinsic fields even though the applied field is very weak. These large fields can and do alter adsorbed species electronic states (e.g., bonding/antibonding orbitals, luminescence, chemical reaction barriers, electron transfer, etc.) as well as rotational and vibrational states. When characterizing fields and voltages in matter, it is essential to specify exactly where they are being evaluated and over what spatial regions of the quantum charge density do different measurements probe (e.g., electron holography tomography vs. vibrational Stark spectroscopies). Here we outline the chemical physics, quantum, and statistical mechanics relevant to these findings and their consequences on how we understand, control, and exploit interfacial fields.

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