

Chemical Analysis and Imaging of Interfaces Room 121 - Session CA-ThA

In Situ and Operando Analysis of Energy and Environmental Interfaces II

Moderators: Ashley Head, Brookhaven National Laboratory, Andrei Kolmakov, National Institute of Standards and Technology (NIST)

2:15pm **CA-ThA-1 Understanding the Molecular Rearrangement at Interface by Atomic Modeling**, *Difan Zhang, D. Heldebrant*, Pacific Northwest National Laboratory; *V. Glezakou, R. Rousseau*, Oak Ridge National Laboratory

INVITED

A fundamental knowledge of the molecular rearrangement at surfaces, gas/liquid, and solid/liquid interfaces is crucial for many applications. The atomic modeling provides an important tool to quantify the structural variation and corresponding property changes at interfaces. In this presentation, I will highlight our recent studies that combined experimental characterization and computational modeling to reveal how molecules rearrange at different interfaces and how such nanostructure changes impact the interfacial properties. For example, the interfacial interactions between the carbon capture solvent and polymer membrane create unique channels that allow for faster diffusion of carbon oxide gas, enhancing the overall performance of the membrane/solvent device. Interestingly, the addition of a small fraction of water molecules further enhances the transport of carbon oxide gas through the membrane/solvent interface. In a different case, atomic modeling also demonstrates the improved selectivity of a graphene-oxide-modified polymer membrane for the separation of organics and water. Overall, these atomic simulations illustrate the effectiveness of modifying interfacial nanostructures to fine-tune interfacial transport and selectivity in complementary to experimental measurements.

2:45pm **CA-ThA-3 Complexity to Clarity: Detecting, Identifying and Analyzing Complex Materials with Machine Learning**, *Paul Pigram, W. Gardner, S. Bamford, D. Winkler*, La Trobe University, Australia; *B. Muir*, CSIRO, Australia; *R. Sun, S. Wong*, La Trobe University, Australia

Our ability to analyze and understand any physical, chemical, or biological material relies on accurately determining its structure, characteristics, and responses. Contemporary analytical techniques produce large volumes of data from pointwise sample analyses (one dimensional (1D) data), maps of compositional distributions (two dimensional (2D) data), and depth profiles showing composition throughout a sample volume (three dimensional (3D) data).

Correlative analyses linking data from the same sample, obtained by different analytical techniques or different operating parameters, are becoming critically important. Different analytical perspectives on the same sample enhance the richness and depth of the conclusions that can be drawn from it.

Recent advances in analytical science have resulted in an overwhelming avalanche of data – the “big data” problem. In our lab a single time-of-flight secondary ion mass spectrometry (ToF-SIMS) experiment might collect a map (512 x 512 pixels) with 2000 mass spectral peaks of significant intensity in 2 – 10 minutes. These half a billion data points all have differing degrees of significance.

In many cases, only a small number of peaks, 10 – 200, may be judged to be characteristic of a specific sample, and the rest of the data may be discarded. However, there are significant risks that such analyses are biased, and may miss important but subtle trends.

There is a very substantial knowledge gap in our ability to find and make full use of the information and knowledge contained in large scale data sets. This gap is driving rapid international progress in the application of materials informatics and machine learning to analytical surface science.

This presentation will highlight our work on applying artificial neural networks, spatial resolution enhancement, computer vision, and related approaches to analysis of a variety of very large hyperspectral data sets to better understand complex materials and their interactions.

3:00pm **CA-ThA-4 Advances in Electron Microscopy for Imaging Surfaces**, *Saumya Mukherjee, S. Böttcher*, SPECS Surface Nano Analysis GmbH, Germany; *K. Kunze*, SPECS Surface Nano Analysis GmbH, Germany, Gibraltar; *O. Schaff*, SPECS Surface Nano Analysis GmbH, Germany

Electron beam-based microscopy faced the challenge of limited accessibility to surface sensitive information and damaging samples owing to the high-kinetic-energy-electron dependent working principle. This led to the development of alternative imaging techniques using low-energy and photo-emitted electrons [1,2]. Photoelectron emission microscopy (PEEM) and Low energy electron microscopy (LEEM) provides the ideal tool to probe surfaces without damaging the sample. Recent advancement in collaboration with Rudolf M. Tromp at IBM, this technique is pushed to produce energy filtered images highlighting its ability for Spectromicroscopy. A lateral resolution below few nanometers is achievable and allowed to measure a wide variety of surfaces. By usage of aperture combinations photoelectrons can be selected within element specific energy range. This provides contrast in images and allows to study delicate biological samples such as imaging of neurons in cells as shown by Boergens et. al [3]. In the present talk, I will discuss in further details the development in surface imaging and complement with results to illustrate the strength of LEEM-PEEM and attract attention of broader imaging community to use this tool beyond conventional electron microscopy on wide variety of sample surfaces.

References:

[1] Ernst Brüche. *Free electrons as probes of the construction of molecules*. In: *Ergebnisse der exakten Naturwissenschaften*. 8 (1929), 185–228.

[2] E. Bauer, “Low energy electron microscopy”, *Rep. Prog. Phys.* 57, 895 (1994).

[3] Kevin M. Boergens, Gregg Wildenberg, Ruiyu Li, Lola Lambert, Amin Moradi, Guido Stam, Rudolf Tromp, Sense Jan van der Molen, Sarah B. King, Narayanan Kasthuri. *Photoemission electron microscopy for connectomics* (bioRxiv 2023.09.05.556423).

3:15pm **CA-ThA-5 The NanoMi Open-source Electron Microscope: Electronics Builds and SEM/STEM Image Generation**, *Darren Homeniuk*, National Research Council, Canada; *M. Kamal*, University of Alberta Edmonton, Canada; *M. Malac, M. Schreiber, M. Salomons*, National Research Council of Canada; *S. Ruttiman*, National Research Council, Canada; *X. Wang*, University of Alberta, Canada; *K. Kwan*, National Research Council of Canada; *O. Adkin-Kaya, J. Calzada*, University of Alberta, Canada; *P. Price, M. Cloutier, M. Hayashida*, National Research Council of Canada; *R. Egerton*, University of Alberta, Canada; *K. Harada*, RIKEN, Japan; *Y. Takahashi*, Hitachi, Ltd., Japan

We are developing a public license electron microscopy platform that we refer to as NanoMi [1,2]. Our goal is for others to be able to build their own version of the platform with minimal money and time invested. The NanoMi platform features modularity in its mechanical and electrical design for adaptability. Further information is available at nanomi.org.

The focus here is to present the electronics builds that support the mechanical hardware. Custom printed circuit boards have been designed, built and tested for the deflectors, beam-shaping stigmators, and piezoelectric movers. The designs were made to be modular, flexible, and cost effective. Through the use of a field-programmable gate array, image generation electronics referred to as a STEM scanner was also created. A first prototype of a custom-built STEM scanner is now complete which provides USB communications to a computer, generation of output X/Y scan signals in 16-bit resolution, simultaneous read-in of 8 14-bit resolution detection signals from the microscope, and an on-board RAM that stores image data until it is ready for transmission. Clock speeds for scanning are 25MHz, which allows the system to acquire samples from the microscope every 40 nanoseconds. A python user interface has been created which allows for settings changes and displays resulting images while allowing the user access to image analysis tools.

Figure 1 shows early results of a 200 mesh copper grid from the new STEM scanner and a comparison image from a simple data acquisition unit, while Figure 2 shows the user interface (UI) during acquisition. Figure 3 shows an image of the board while acquiring Figure 1.

Acknowledgment:Support for the project was provided by NRC-NANO and by NSERC RGPIN-2021-02539

Thursday Afternoon, November 7, 2024

References:

- [1] nanomi.org and <https://github.com/NRC-NANOMi/NanoMi>
[2] M. Malac et. al, NanoMi: An open source electron microscope hardware and software platform, *Micron* **163** (2022) 103362.

3:30pm CA-ThA-6 Advancing Carbon Dioxide Removal Technologies with Microscopic Insights Gained Using in-Situ and Operando Transmission Electron Microscopy, Wei-Chang David Yang, National Institute of Standards and Technology (NIST) INVITED

Carbon dioxide removal is crucial for achieving net-zero emissions and mitigating climate change. Still, technological challenges like inconsistent sorbent performance and catalyst degradation hinder the deployment of carbon dioxide capture and conversion to value-added products [1,2]. Transition metals (Ni, Co, Fe), which catalyze CO₂ conversion into hydrocarbon fuels, face deactivation (coking) due to carbon deposition on the catalyst surface [3]. Burning off the carbon deposit coarsens the catalyst and deteriorates performance, highlighting the need for a nonthermal regeneration process. Meanwhile, many mesoporous sorbents impregnated with amine-based polymers for direct air capture show inconsistent performance in the literature [4], requiring high-spatial-resolution multimodal characterization for benchmarking from single pores to overall performance.

This talk covers how in-situ and operando methods developed for an environmental transmission electron microscope (ETEM) address the above issues. Firstly, we used an electron beam to excite and characterize localized surface plasmon (LSP) resonance on aluminum nanoparticles in the presence of CO₂ using in-situ electron energy-loss spectroscopy (EELS). LSP field enhancement in the ultraviolet (UV) spectral range boosted the reverse Boudouard reaction (RBR), consuming carbon deposits and reactivating transition metal catalysts without heating.[5] We also coupled a TEM gas cell holder to gas chromatography-mass spectrometry (GC-MS) for operando detection of CO produced during the reaction, which can be reused for hydrocarbon fuel production. The findings offer a new solution for regenerating catalysts in CDR technology.

The second part of the talk focuses on developing in-situ cryogenic EELS imaging to characterize the adsorption ability of individual mesopores. The energy-loss near-edge structure (ELNES) obtained at cryogenic conditions showed the carbonyl core to $\pi^*_{C=O}$ transition (≈ 289 eV) in ammonium carbamate [6], indicating the formation of chemisorbed species when exposed to dry CO₂. This is the first direct observation of CO₂ chemisorption on amine-impregnated mesoporous silicas at the single pore level. Ongoing studies aim to elucidate the amine chemistry and kinetics exposed to CO₂ within the mesopores.

References:

- [1] S. Choi, J. H. Drese, and C. W. Jones, *ChemSusChem* **2** (2009), p. 785.
[2] R. W. Dornier et al., *Energy Environ. Sci.* **3** (2010) p. 884.
[3] M. D. Argyle and C. H. Bartholomew, *Catalysts* **5** (2015), p. 145.
[4] J. Wu et al., *Chem. Eng. J.* **450** (2022), p. 137958.
[5] C. Wang et al., *Nat. Mater.* **11** (2019), p. 47037.
[6] W. G. Urquhart and H. Ade, *J. Phys. Chem. B* **106** (2002), p. 8531.

4:00pm CA-ThA-8 In situ Photoelectron and Infrared Spectroscopic Studies of Materials Under Various Plasmas, Ashley Head, Brookhaven National Laboratory; T. Hu, Brookhaven National Laboratory and State University of New York at Stony Brook; A. Boscoboinik, D. Stacchiola, Brookhaven National Laboratory

Non-thermal plasma has been used to functionalize materials, to enhance the deposition of films, and as a reactant in catalysis. Depending on how plasma is made, there can be a range of gaseous species. Tools are needed for in situ studies in plasmas environments to understand the interactions with materials.^{1,2} The application of infrared reflection absorption spectroscopy (IRRAS) and ambient pressure X-ray photoelectron spectroscopy to plasma environments will be discussed. As an example system, the functionalization and reduction of HKUST-1, a Cu-based metal-organic framework, has been studied with these techniques. IRRAS follows the framework stability while APXPS follows the Cu oxidation state changes. This correlative methodology is being baselined for future studies of plasma-enhanced catalysis of MOFs and metal oxides.

1. G. Li, D.N. Zakharov, S. Sikder, Y. Xu, X. tong, P. Dimitrakellis, J.A. Boscoboinik, *Nanomaterials*, **2024**, *14*, 290.
2. J.T. Diulus, A.E. Naclerio, J.A. Boscoboinik, A.R. Head, E. Strelcov, P.R. Kidambi, A. Kolmakov, *J. Chem. Phys. C* **2024**, *128*, 7591.

4:15pm CA-ThA-9 Chemical and Morphological Stability of Diamond Device Interfaces Under Operando Plasma-XPS, J. Trey Diulus, NIST-Gaithersburg; A. Head, J. Boscoboinik, Center for Functional Nanomaterials, BNL; A. Kolmakov, NIST-Gaithersburg

Device fabrication of field effect transistors (FETs) and other electronics are still largely dependent on Si, which has been the core semiconductor material for over seven decades. Alternatively, diamond is a promising semiconductor material, with its ultra-wide bandgap (5.5 eV), unmatched thermal conductivity, breakdown voltage, and high charge carrier mobility in the range of 1000 cm² V⁻¹ s⁻¹, while offering improved chemical stability compared to other wide-bandgap alternatives, like SiC and GaN. However, surface hydrogenation via H₂ plasma is necessary to fabricate high-mobility diamond FETs, and the resulting surface is sensitive to ambient adsorbates that deteriorate the stability of surface conductivity with modern manufacturing processes. Alternatively, introducing the hydrogenation step later in the manufacturing process, i.e. after deposition of metal contacts or the gate dielectric, could allow for improved control of the diamond/metal or diamond/metal-oxide interfaces. Recently, high resolution x-ray photoelectron spectroscopy (XPS) collected under plasma conditions has been reported, allowing for *operando* chemical stability measurements. Herein, we prepared un-doped diamond and B-doped diamond samples with the standard contact metal stack (Ti/Pt/Au) deposited on half of the samples for plasma-XPS in H₂ and O₂ plasmas, respectively. Interestingly, a significant shift of ~ 50 eV to higher binding energy is seen in the XPS spectra of the un-doped diamond when a plasma is ignited at 13 Pa partial pressure of H₂ that is not seen in the spectra for the metalized part in the same environment. Additionally, the B-doped diamond exposed to the same pressure of an O₂ plasma also does not exhibit a shift of the same magnitude as the un-doped diamond in H₂. The insulating nature of un-doped diamond creates this significant charging effect seen by XPS, which varies with the surface conductivity of diamond, suggesting a potential route to estimate the conductance state of diamond. Furthermore, with *ex situ* scanning electron microscopy, we see significant erosion in the Au coated surface that is exposed to H₂ plasma, likely due to a sputtering effect from ion impingement. Evidence of parasitic reactions from chamber wall exposure is also seen from residual gas analysis. This stresses the importance of designing a plasma that minimizes ions but maximizes neutrals, while also utilizing a well-cleaned chamber with minimal surface area to avoid scrubbing the chamber during plasma exposure. Overall, our efforts aim to better understand the interaction of plasma with diamond to provide researchers with a streamlined route towards diamond device manufacturing.

Author Index

Bold page numbers indicate presenter

— A —

Adkin-Kaya, O.: CA-ThA-5, 1

— B —

Bamford, S.: CA-ThA-3, 1

Boscoboinik, A.: CA-ThA-8, 2

Boscoboinik, J.: CA-ThA-9, 2

Böttcher, S.: CA-ThA-4, 1

— C —

Calzada, J.: CA-ThA-5, 1

Cloutier, M.: CA-ThA-5, 1

— D —

Diulus, J.: CA-ThA-9, 2

— E —

Egerton, R.: CA-ThA-5, 1

— G —

Gardner, W.: CA-ThA-3, 1

Glezakou, V.: CA-ThA-1, 1

— H —

Harada, K.: CA-ThA-5, 1

Hayashida, M.: CA-ThA-5, 1

Head, A.: CA-ThA-8, 2; CA-ThA-9, 2

Heldebrant, D.: CA-ThA-1, 1

Homeniuk, D.: CA-ThA-5, 1

Hu, T.: CA-ThA-8, 2

— K —

Kamal, M.: CA-ThA-5, 1

Kolmakov, A.: CA-ThA-9, 2

Kunze, K.: CA-ThA-4, 1

Kwan, K.: CA-ThA-5, 1

— M —

Malac, M.: CA-ThA-5, 1

Muir, B.: CA-ThA-3, 1

Mukherjee, S.: CA-ThA-4, 1

— P —

Pigram, P.: CA-ThA-3, 1

Price, P.: CA-ThA-5, 1

— R —

Rousseau, R.: CA-ThA-1, 1

Ruttiman, S.: CA-ThA-5, 1

— S —

Salomons, M.: CA-ThA-5, 1

Schaff, O.: CA-ThA-4, 1

Schreiber, M.: CA-ThA-5, 1

Stacchiola, D.: CA-ThA-8, 2

Sun, R.: CA-ThA-3, 1

— T —

Takahashi, Y.: CA-ThA-5, 1

— W —

Wang, X.: CA-ThA-5, 1

Winkler, D.: CA-ThA-3, 1

Wong, S.: CA-ThA-3, 1

— Y —

Yang, W.: CA-ThA-6, 2

— Z —

Zhang, D.: CA-ThA-1, 1