Nanoscale Science and Technology
Room 206 A W - Session NS2+2D-TuM

Multimodal Techniques in Surface and Interface Engineering at the Nanoscale

Moderators: Aubrey Hanbicki, Laboratory for Physical Sciences, **Mausumi Mahapatra**, Loyola University Chicago

9:15am **NS2+2D-TuM-6 On-Surface Synthesis on Inert and Reactive Surfaces**, *Rafał Zuzak, **Szymon Godlewski**,* Jagiellonian University, Poland

In recent years the on-surface manipulation and chemical reactions created a playground for atomically precise synthesis and development of new atomic and molecular nanostructures. However, the abilities to produce desired systems are limited, among others, by relying on the catalytic role of the substrate in initiating selected reactions. Therefore striving for the generation of desired systems forces the search of new reaction pathways and catalytic transformations.

In this talk I will demonstrate our approach based on the application of inert and reactive surfaces in the on-surface experiments. First, I will discuss the synthesis of the acene series with the first observation of spin excitation recorded for tridecacene [1]. Subsequently the focus will be shifted toward non-metallic substrates and the new pathway for the synthesis of new molecular compounds [2] with prospects for circumventing the need to exploit the catalytic role of metallic substrates [3]. Finally, concepts for on-surface reactions on chemically active lithium substrates will be presented. They will be focused on preventing catastrophic dendrite formation in battery electrodes.

The research was supported by the National Science Center, Poland: 2019/35/B/ST5/02666, 2022/04/Y/ST5/00156.

References

[1] R. Zuzak et al., *Angew. Chem. Int. Ed.*, **63**, e202317091 (2024)

[2] R. Zuzak et al., *ACS Nano*, **17**, 2580-2587 (2023)

[3] R. Zuzak et al., *Nat. Commun.* **16**, 691 (2025)

9:30am **NS2+2D-TuM-7 Generalized Defect Quantification of 2D Materials with Atomic Force Microscopy**, ***Matthew Rosenberger,*** University of Notre Dame **INVITED**

Routine defect characterization is a critical capability for understanding defect-property correlations and optimizing growth of two-dimensional (2D) materials. High throughput optical methods for defect characterization, such as Raman spectroscopy, are useful for graphene, but are insufficiently sensitive to defects in some other 2D materials, such as transition metal dichalcogenides (TMDs), particularly for defect densities of about 10^{12} cm^{-2} or less. Typical methods for directly detecting defects at the atomic scale, such as scanning transmission electron microscopy (STEM) and scanning tunneling microscopy (STM), are effective, but they are slow and often require arduous sample preparation. There is a need for 2D material defect characterization techniques that are routine, fast, and reliable. Here, we demonstrate two atomic force microscopy (AFM)-based techniques for locating and quantifying atomic-scale defects in 2D materials. First, we show that conductive AFM can locate and differentiate the same defects as STM by comparing conductive AFM and STM on the same region of a TMD crystal[1]. Our work establishes conductive AFM as a higher-throughput alternative to STM for defect quantification. Second, we show that lateral force microscopy (LFM) can locate atomic-scale defects through a direct comparison of LFM with conductive AFM on a TMD crystal[2]. Importantly, we show that LFM can locate atomic-scale defects in TMD monolayers on insulating substrates and in insulating 2D materials, such as hexagonal boron nitride, because LFM is a purely mechanical technique. The AFM-based methods presented here enable routine defect characterization, which will facilitate rapid investigations of defect-property relationships and speed up the development of new growth processes.

(1) Xu, K.; Holbrook, M.; Holtzman, L. N.; Pasupathy, A. N.; Barmak, K.; Hone, J. C.; Rosenberger, M. R. Validating the Use of Conductive Atomic Force Microscopy for Defect Quantification in 2D Materials. *ACS Nano* **2023**, *17* (24), 24743–24752. https://doi.org/10.1021/acsnano.3c05056.

(2) Yang, Y.; Xu, K.; Holtzman, L. N.; Yang, K.; Watanabe, K.; Taniguchi, T.; Hone, J.; Barmak, K.; Rosenberger, M. R. Atomic Defect Quantification by Lateral Force Microscopy. *ACS Nano* **2024**, *18* (9), 6887–6895. https://doi.org/10.1021/acsnano.3c07405.

11:00am **NS2+2D-TuM-13 Excess Barrier Height Unlocks Andreev Reflection in Scanning Tunneling Microscopy**, ***Petro Maksymovych,*** Clemson University; *Wonhee Ko,* University of Tennessee Knoxville; *Jose Lado,* Aalto University, Finland

Superconductors are currently entering a new golden age, marked by a renewed quest for higher Curie temperature, explosion of new candidate superconducting materials and emerging applications, such as topological quantum computing. However, the foundational questions—whether the material is actually superconducting and what causes superconductivity—remain as pertinent as ever. Indeed, pairing symmetry—a key property of any superconductor—can be a challenging and contested property, even for materials where superconductivity itself is unambiguous.

To this end, we introduced a new approach to detect Andreev reflection (AR) in metal-superconducting contacts of arbitrarily high resistance, most notably in scanning tunneling microscopy (STM). Fundamentally, AR allows the injection of Cooper pairs from a metal to a superconductor, producing excess conductance and a unique sensitivity to the properties of a superconducting state. However, detecting AR in traditional transport measurements requires low (ideally zero) contact resistance —limiting its application to mesoscale and contact geometries. To remove this limitation, we shifted the experimental observable from the excess conductance to the excess height of the tunneling barrier, providing a new approach to detect, probe, and quantify Andreev reflection.

In this talk, I will discuss how tunneling barrier height spectroscopy functions in superconducting junctions and present our recent computational and experimental results on AR-STM with both conventional and unconventional superconductors. The barrier height spectroscopy has a rich structure with combined sensitivity to the pairing symmetry, number of superconducting gaps and the detailed structure of the Fermi surface. Moreover, excess barrier height detects special, higher order Andreev reflection processes, that occur in proximate tunneling junctions just before the collapse of the tunneling barrier. As a result, STM can now leverage the unique power of Andreev reflection to probe superconductivity, magnetism and even topological properties from a new perspective. Research sponsored by Clemson University and US Department of Energy. SPM experiments were carried at the Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, a US DOE User Facility. Song/PM, arXiv: 2411.11724; Ko/PM. Nano Letters, **2023** *23* (17), 8310-8318; Song/PM, *Nano Letters* **2023** *23* (7), 2822-2830; Ko/PM, *Nano Letters* **2022** *22* (10), 4042-4048

11:15am **NS2+2D-TuM-14 Dynamic Evolution of Rh/Fe_3O_4(001) Catalysts Under Hydrogen Conditions**, ***Mausumi Mahapatra,*** Loyola University Chicago; *Marcus Sharp, Zdenek Dohnalek, Christopher Lee, Yifeng Zhu, Oliver Gutiérrez, Bruce Kay,* Pacific Northwest National Laboratory

Metal/oxide interfaces are a new emerging class of catalysts owing to their unique electronic and chemical properties. In this study, we have prepared a series of model Rh/Fe_3O_4(001)catalysts that include Rh adatoms (Rh_{ad}), mixed surface layers with octahedrally-coordinated Rh (Rh_{oct}), as well as metallic Rh clusters and nanoparticles (Rh_{met}) on Fe_3O_4(001). Using X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM), we investigated the activity of such model systems towards H_2 and their stability in reducing environments. Our results show that the atomically dispersed Rh_{ad} and Rh_{oct} species do not activate H_2, which would result in the formation of surface hydroxyls on Fe_3O_4(001). In contrast, the presence of Rh_{met} in H_2 results in the formation of hydroxyls and subsequent etching of the Fe_3O_4(001) at higher temperatures (≥ 500 K) due to water formation via the Mars−van Krevelen mechanism. Additionally, such surface etching leads to the release of the Rh_{oct} from the surface lattice and their sintering to Rh_{met}. To bridge the material gap between the model and high surface area catalysts, we perform parallel studies on powder Rh/Fe_3O_4 catalysts. The XPS characterization shows remarkable similarities between these systems. Further, our model studies provide an atomistic picture of the behavior of high surface area catalysts in the H_2 atmosphere.

11:30am **NS2+2D-TuM-15 Hybrid ALD-MLD HfOx Thin Films: The Role of Carbon for Memristive Application**, ***Soham Shirodkar,*** *Dushyant Narayan, Minjong Lee, Dan Le,* University of Texas at Dallas; *Jacob N. Rohan,* Cerfe Labs, Austin; *Jiyoung Kim,* University of Texas at Dallas

Resistive switching (RS) memories based on transition metal oxides (TMOs) are a promising class of emerging nonvolatile memory devices for next-generation electronics. However, conventional TMO-based RS memories typically require high forming voltages (V_{form}) during initial operation, consuming excessive power. To address this issue, incorporation of metal dopant species into TMOs is proposed to lower the V_{form} [1]. For example, Hf/Zr doping in TiO_2 ReRAM has been demonstrated to increase the formation of oxygen vacancies, leading to lower forming voltages [2]. In our previous work, we have demonstrated that incorporating carbon into HfO_x films via a hybrid Atomic Layer Deposition (ALD)/Molecular Layer Deposition (MLD) process can eliminate the need for a forming process, enabling 'Born-ON' behavior during the first sweep [3,4]. However, control of carbon incorporation is challenging due to its high atmospheric reactivity. Therefore, the choice of organic precursor during the MLD can significantly influence the film's properties and ultimately the device properties.

In this work, we systematically investigate the impact of different organic precursors during ALD/MLD hybrid process using two linear-chain hydrocarbons Ethylene Glycol (EG) and Glycerol (GL) as well as an aromatic hydrocarbon Hydroquinone (HQ). These organic precursors vary in number of carbon atoms and number and position of OH groups. In this regard, we observed significant differences in growth per cycle (GPC) and carbon bonding states: HQ, being the largest molecule, exhibited the highest GPC-3.1 Å/cycle and carbon composition-45% along with higher expected C-sp^2 content due to its aromaticity. Whereas EG showed a low GPC-0.2 Å/cycle and less carbon incorporation-15% due to its small size and possible poisoning effects. In contrast, GL, with an additional OH group, likely mitigates these poisoning effects common to linear hydrocarbons, resulting in a GPC of 2.1 Å/cycle and 31% carbon content. Metal-Insulator-Metal devices with these films exhibit distinct 'Born-ON' behavior as well as resistive switching without electroforming, though each precursor-based film requires a different thermal budget to activate this response. This study underscores the crucial role of precursor chemistry in tailoring the properties of carbon-doped TMO memristors and offers potential pathways for improving RS device performance.

This research is supported by Cerfe Labs and Air Force Research Laboratories.

[1] H.-S. Philip Wong et al., J Electroceram (2017) 39:21-38

[2] Yoshio Nishi et al., *ICSSDM, Kyoto* (2012)

[3] C. A. Paz de Araujo et al., *APL Mater.* **10**, 040904 (2022)

[4] M. Lee et al., *ALD/ALE* (2024)

11:45am **NS2+2D-TuM-16 Quantitative Comparative Force Spectroscopy on Molecules***, Xinzhe Wang,* Yale University*; Percy Zahl,* Brookhaven National Laboratory*; Jara Trujillo Mulero,* Universidad Autonoma de Madrid, Spain*; Hailiang Wang,* Yale University*; Rubén Pérez,* Universidad Autonoma de Madrid, Spain*; Eric Altman,* ***Udo Schwarz****,* Yale University

Understanding molecular-scale interactions at surfaces is essential for advancing catalyst design and developing efficient energy conversion processes. Here, we report ongoing efforts to improve the spatial accuracy and quantitative reliability of three-dimensional atomic force microscopy (3D-AFM) by refining data correction techniques for CO-functionalized tips. These developments allow us to minimize tip- and substrate-induced artifacts and isolate the intrinsic molecular interaction at atomic resolution.

As a testbed for this approach, we investigate cobalt phthalocyanine (CoPc) and its amino-functionalized counterpart ($(NH_2)_4$CoPc) adsorbed on Ag(111), both of which are of interest in CO_2 electroreduction catalysis. By identifying and removing asymmetric force contributions caused by the metallic structure of the tip, we obtain corrected force spectroscopy data that reveal equilibrium interaction distances and energies across individual molecules. Our analysis shows that NH_2 substitution alters the spatial distribution of interaction strength, decreasing equilibrium distances near ligand attachment points while broadly reducing interaction energy with the tip.

These experimental observations agree well with DFT-based simulations and suggest that side-group functionalization directly modulates the molecule's chemical landscape. The methodology provides a direct route toward correlating molecular structure with catalytic behavior at the single-molecule level, thereby enabling a deeper understanding of functional molecular systems on surfaces.

12:00pm **NS2+2D-TuM-17 Thermal Strain-Induced Nanogap Formation in Monolayer MoS_2 during CVD Growth***,* ***Seonha Park****, Sieun Jang, Songkil Kim,* School of Mechanical Engineering, Pusan National University, Republic of Korea

Molybdenum disulfide (MoS_2) is a promising semiconducting material due to its atomic flatness and high carrier mobility. In particular, chemical vapor deposition (CVD)-grown MoS_2 has been widely explored for electronic applications owing to its high quality and scalability. However, the mismatch in thermal expansion coefficients between MoS_2 and the growth substrate induces strain in MoS_2 flakes, and the nanogap structure can be formed to release such growth-induced strain. Understanding and controlling this unique nanogap structure is of great interest, as it offers opportunities for applications such as nanogap electrodes, biosensors, and gas sensors. In this work, nanogap formation mechanisms and the factors governing gap size and morphology were systematically investigated in monolayer CVD MoS_2. To investigate the role of MoS_2–substrate interfacial bonding strength in nanogap formation, three samples with different adhesion properties with the substrate are prepared. Strain distribution analysis using photoluminescence (PL) mapping and statistical analysis of multiple SEM images revealed that interfacial bonding strength significantly affects strain relaxation behavior, where weaker bonding facilitates strain release, leading to faster crack propagation and more irregular gap paths. The crystallographic configuration also influenced propagation behavior. Asymmetric bi-crystalline flakes with misorientation angles showed a stronger tendency for cracks to follow grain boundaries due to increased mechanical instability. Additionally, the relationship between flake size and nanogap size was also investigated. In samples with moderate interfacial bonding strength, a linear increase in nanogap size was observed with increasing flake size above a critical threshold. In contrast, strongly bonded samples exhibited smaller nanogaps than the moderate bonding sample, with minimal variation in gap size regardless of flake size. These results suggest that nanogap size can be effectively controlled by tuning the interfacial bonding strength and the flake size.

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