

Surface Science Division

Room 319 - Session SS+2D+AS-TuA

Structure, Adsorption and Reaction at 2D Material Surfaces

Moderators: Florencia C. Calaza, Instituto de Desarrollo Tecnológico para la Industria Química, Argentina, Arthur Utz, Tufts University

2:20pm **SS+2D+AS-TuA-1 Chemically Identifying Single Adatoms with Single-Bond Sensitivity During Oxidation Reactions of Borophene**, L. Li, N. Jiang, *Sayantana Mahapatra*, University of Illinois - Chicago

The chemical interrogation of individual atomic adsorbates on a surface significantly contributes to understanding the atomic-scale processes behind on-surface reactions. However, it remains highly challenging for current imaging or spectroscopic methods to achieve such a high chemical spatial resolution. Here we show that single oxygen adatoms on a boron monolayer (i.e., borophene) can be identified and mapped via ultrahigh vacuum tip-enhanced Raman spectroscopy (UHV-TERS) with ~ 4.8 Å spatial resolution and single bond (B–O) sensitivity. With this capability, we realize the atomically defined, chemically homogeneous, and thermally reversible oxidation of borophene via atomic oxygen in UHV. Furthermore, we reveal the propensity of borophene towards molecular oxygen activation at room temperature and phase-dependent chemical properties. In addition to offering atomic-level insights into the oxidation of borophene, this work demonstrates UHV-TERS as a powerful tool to probe the local chemistry of surface adsorbates in the atomic regime with widespread utilities in heterogeneous catalysis, on-surface molecular engineering, and low-dimensional materials.

2:40pm **SS+2D+AS-TuA-2 Tailoring the Interfacial Properties of 2D Transition Metal Silicates on Metal Supports**, N. Doudin, K. Saritas, Yale University; J. Boscoboinik, G. Li, Brookhaven National Laboratory; S. Ismail-Beigi, Eric Altman, Yale University

Two-dimensional (2D) transition metal (TM) silicates have the potential to add magnetic, piezoelectric, and multiferroic functionalities to the toolkit of 2D layers used to develop new technologies. To date, these 2D TM silicates have been chemically bound to the growth substrate through oxygen atoms; the ability to weaken the interaction with the substrate to isolate the materials as single vdW layers is crucial for realizing their potential. Hydration or hydrogenation of the 2D TM silicate presents an ideal modification methodology to pacify the bonds to the substrate and create tailored interface properties and functionalities. Towards this end, here we report the interaction of Au- and Pd-supported 2D TM silicates with H₂O, H₂, and O₂. We employed a range of characterization tools to assess the materials before and after treatment with the probe molecules. Ambient pressure x-ray photoelectron spectroscopy (AP-XPS), ambient pressure infrared reflection absorption spectroscopy (AP-IRRAS), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM) in conjunction with first principles theory were utilized to assess surface morphology, interface characteristics, surface chemistry, and chemistry in the confined spaces between the 2D TM silicate and metal support. The interaction of probe molecules with TM silicates on Pd(111) and Au(111) was studied over wide pressure (10^{-6} –1 mbar) and temperature (300–600 K) ranges. The data show that the dissociative adsorption of H₂ takes place to form OH bonds on the oxide surfaces under UHV conditions. When the pressure is increased to several mbar, the metal silicate surfaces are saturated with H atoms at 300 K. Exposure to H₂ at higher surface temperatures (≥ 600 K) reduces the TM silicate. Also, water dissociates readily on the metal silicate surfaces at 300 K. With an increase in H₂O pressure, a greater degree of surface hydroxylation was observed for all samples. At 1 mbar H₂O, molecular and dissociated water coexist (hydrogen bond OH/H₂O). In temperature-dependent studies, desorption of weakly bound water and surface dehydroxylation were observed with increasing temperature. Via AP-XPS combined with IRAS we study in detail the interaction of oxygen with the oxide surfaces, which shows that H₂-induced reduction can be reversed and the original structure restored. Our studies provide an effective avenue to achieve hydrated metal silicate layers and shed light on how to tune the chemical reactions of these overlayers by choosing suitable substrates.

3:00pm **SS+2D+AS-TuA-3 Metal Oxide and Metal Dichalcogenide 2D Nanocrystals: Structure, Adsorption and Catalytic Properties**, Jeppe V. Lauritsen, Aarhus University, Denmark

INVITED

Nanocrystals of two-dimensional materials may exhibit fascinating optical, electronic or chemical properties. In heterogeneous catalysis, the edge

sites of some planar metal oxide and metal sulfide nanocrystals have been demonstrated to be far more active than the majority sites exposed on basal planes. These observations have motivated us to obtain a better understanding of the edge site structure of 2D nanocrystals and try to establish the fundamental connection to their behavior in heterogeneous catalysis and electrocatalysis. I will discuss two examples showing how we investigated the structure and adsorption properties at the atomic scale by using scanning tunneling microscopy (STM) and photoemission spectroscopy techniques (XPS) on well-defined planar 2D nanocrystals supported on model substrates:

i. We used atom-resolved STM images to investigate edge reactivity of monolayer CoOOH_x particles, widely considered as the active phase of cobalt-based catalysts in alkaline electrochemical water splitting. Water exposure experiments combined with atom-resolved STM imaging directly show an increased capacity to dissociate water on the edge sites, which is further substantiated by theoretical modelling [1]. Moreover, addition of Fe has a strong promotional effect on the oxygen evolution. We have compared how the CoOOH_x nanocrystals and chemical composition develop after the sample has been used as the working model electrode directly in a homebuilt *in situ* electrochemical cell attached to the STM chamber [2]. Our activity measurements confirm the expected increased oxygen evolution (OER) activity for Co-oxides mixed with Fe, which however depends in a highly non-linear way on the actual Fe content. Based on this information we found a model where the main effect of Fe doping in Co oxide is that of a structural edge stabilizer [3].

ii. MoS₂ nanocrystals are active catalysts in heteroatom extrusion from hydrocarbons (O, N, S) in oil and bio-oil processing (hydrotreating). Atom-resolved STM studies of MoS₂ nanocrystals as a supported model catalysts was used in combination with DFT analysis of molecule adsorption on MoS₂ edge to evidence an interesting new mechanism where adsorption of heteroatom-bearing hydrocarbons on a vacancy pushes neighboring S atoms aside. Thereby the adsorption event itself creates better catalytic active sites capable of adsorbing large hydrocarbons, explained the unusually wide selectivity of MoS₂ towards these reactions [4].

[1] J. Fester, et al., Nat. Comm **8**, 14169 (2017).

[2] Z. Sun, et al., Rev. Sci. Inst. **92**, 094101 (2021).

[3] Z. Sun, et al., ACS Nano **15**, 18226 (2021).

[4] N. Salazar, et al., Nat. Comm **11**, 4369 (2020).

4:20pm **SS+2D+AS-TuA-7 Intercalated Cu₂O Thin Film Confined Underneath Hexagonal Boron Nitride**, J. Trey Diulus, Z. Novotny, N. Dongfang, N. Comini, J. Beckord, Y. Al-Hamdani, University of Zurich, Switzerland; M. Muntwiler, Paul Scherrer Institute, Switzerland; M. Hengsberger, M. Iannuzzi, J. Osterwalder, University of Zurich, Switzerland

Confined catalysis has been achieved in zero and one dimensions using zeolites, metal-organic frameworks, and carbon nanotubes for optimized catalytic performance. Confinement can also be achieved in two dimensions by intercalation of reactants between solid layers. 2D materials grown on metal surfaces have become widely used model systems to study 2D-confined catalysis. Yet, numerous transition metals have been found to be more active in their oxidized form. Unfortunately, the growth of h-BN via chemical vapor deposition (CVD) has proven to be more difficult on metal oxides than on metals. Instead, a metal substrate underneath an h-BN monolayer can be oxidized via O₂ intercalation. Due to weak interactions between h-BN and Cu(111), the Cu(111) substrate is a prime candidate for intercalated oxidation, forming a thin oxide film (~ 3 Å) while the h-BN remains intact. Growth of h-BN on Cu(111) was achieved through CVD by borazine exposure in ultra-high vacuum at the In Situ Spectroscopy beamline at the Swiss Light Source (SLS). The surface structure, chemical composition, and uniformity of the as-grown h-BN/Cu(111) heterostructure were determined with low-energy electron diffraction, Auger electron spectroscopy, and X-ray photoelectron spectroscopy (XPS). Oxidation of the Cu(111) under h-BN via O₂ intercalation was executed by exposure to near-ambient partial pressures of O₂ (0.001 to 1 mbar) at temperatures ranging from 25 to 200 °C. Ambient pressure XPS and X-ray absorption spectroscopy were utilized at each temperature and pressure to determine the oxidation state of Cu and develop a recipe for preparing an ordered h-BN/Cu₂O/Cu(111) heterostructure. Further characterization of an ordered h-BN/Cu₂O/Cu(111) was obtained at the PEARL beamline at the SLS. Scanning tunneling microscopy (STM) provided atomic-resolution imaging of the sample held at 78 K, displaying a Cu₂O-like structure. STM further shows the oxidation of the Cu(111) substrate occurs via O intercalation at the h-BN grain boundaries. Density functional theory calculations, X-ray photoelectron diffraction experiments, and multiple-scattering simulations

Tuesday Afternoon, November 8, 2022

using the Electron Diffraction in Atomic Clusters code, provided further structural information, suggesting O atoms first adsorb to HCP-Cu sites on Cu(111), followed by the formation of a Cu₂O-like trilayer in between the substrate and h-BN. Ultimately, we fully characterize the structure and oxidation mechanism of a well-defined nano-reactor system that is ideally suited to study reactions in confined space. Furthermore, we propose this preparation method can be applied to more systems comprising of a 2D monolayer on a metal substrate.

4:40pm **SS+2D+AS-TuA-8 Imaging Surface Defects on MoS₂**, *Blake Birmingham*, Baylor University

MoS₂ is an exciting hydrogen evolution reaction (HER) catalyst that exhibits promising activity in acidic media. However, the role of density and reactivity of defect sites to the HER performance of MoS₂ is currently unclear. Up to now, correlation of localized HER activity to atomic scale defects have been inferred via ex-situ measurements, where the macroscopic electrode activity is determined via bulk electrochemical techniques and correlated with the number of active sites that are measured separately via nanoscale surface imaging such as Scanning Tunneling Microscopy (STM) or Transmission Electron Microscopy.

In the presented experiment, the structural and chemical properties of bulk mineral MoS₂ catalyst during HER were monitored in-situ by electrochemical scanning tunneling microscopy (EC-STM). The nanoscale structure of the MoS₂ is correlated with its electrochemical activity in 0.5 M H₂SO₄(aq) electrolyte. Defects on the MoS₂ basal plane were atomically resolved before and after several rounds of cyclic voltammetry (CV) measuring the HER current vs applied potential against a carbon reference. Atomically resolved imaging of the same nanoscale area before and after HER does not show an increase in atomic defect site density after prolonged HER probed by many rounds of CVs. This indicates that new sulfur vacancies are either not produced during HER on MoS₂ basal plane or are produced and immediately occupied by hydrogen atoms. The surface was imaged near the HER onset potential, the evolution reaction was directly imaged as strong local tunneling instability. The tunneling destabilization effect is strongest near the nanoscale defect sites potentially due to local hydrogen gas bubbling.

5:00pm **SS+2D+AS-TuA-9 Modifying 2D Transition Metal Dichalcogenides (TMDs) by Incorporating Excess Transition Metals**, *Matthias Batzill*, University of South Florida **INVITED**

Crystal modifications in 2D materials can introduce new functionalities in these materials. Here we discuss compositional and structural crystal modifications in some transition metal dichalcogenides (TMDs). Specifically, we show that excess metals can be incorporated into the crystal structures of Mo-, and W- dichalcogenides and in PtTe₂. In the former the excess metals result in the formation of metal rich mirror twin grain boundary networks, while in the latter a phase transition from PtTe₂ to Pt-monotelluride can be induced. In this presentation we discuss the transformation mechanisms and the properties that arise from these compositional modifications.

5:40pm **SS+2D+AS-TuA-11 SSD Flash Poster Session: Oral Presentations**

5:40: SS-TuP-7 - Dr. Pierluigi Bilotto

5:43: SS-TuP-12 - Dr. Benjamin Reed

5:46: SS-TuP-13 - Mr. Xiao Zhao

5:49: SS-TuP-6 - Dr. J. Trey Diulus

5:52: SS-TuP-9 - Mr. Dustin Johnson

5:55: SS-TuP-18 - Aman Patel

Author Index

Bold page numbers indicate presenter

— A —

Al-Hamdani, Y.: SS+2D+AS-TuA-7, **1**

Altman, E.: SS+2D+AS-TuA-2, **1**

— B —

Batzill, M.: SS+2D+AS-TuA-9, **2**

Beckord, J.: SS+2D+AS-TuA-7, **1**

Birmingham, B.: SS+2D+AS-TuA-8, **2**

Boscoboinik, J.: SS+2D+AS-TuA-2, **1**

— C —

Comini, N.: SS+2D+AS-TuA-7, **1**

— D —

Diulus, J.: SS+2D+AS-TuA-7, **1**

Dongfang, N.: SS+2D+AS-TuA-7, **1**

Doudin, N.: SS+2D+AS-TuA-2, **1**

— H —

Hengsberger, M.: SS+2D+AS-TuA-7, **1**

— I —

Iannuzzi, M.: SS+2D+AS-TuA-7, **1**

Ismail-Beigi, S.: SS+2D+AS-TuA-2, **1**

— J —

Jiang, N.: SS+2D+AS-TuA-1, **1**

— L —

Lauritsen, J.: SS+2D+AS-TuA-3, **1**

Li, G.: SS+2D+AS-TuA-2, **1**

Li, L.: SS+2D+AS-TuA-1, **1**

— M —

Mahapatra, S.: SS+2D+AS-TuA-1, **1**

Muntwiler, M.: SS+2D+AS-TuA-7, **1**

— N —

Novotny, Z.: SS+2D+AS-TuA-7, **1**

— O —

Osterwalder, J.: SS+2D+AS-TuA-7, **1**

— S —

Saritas, K.: SS+2D+AS-TuA-2, **1**