Monday Afternoon, November 7, 2022

Surface Science Division
Room 319 - Session SS+AS-MoA

Molecular Organization at Surfaces

Moderator: Donna Chen, University of South Carolina

2:40pm SS+AS-MoA-4 Protein Structure and Dynamics at the Air-Water Interface Using Sum Frequency Generation Simulations, *Kris Strunge,* Aarhus University, Denmark*; Y. Nagata,* Max Planck Institute for Polymer Research, Germany, Denmark*; T. Weidner,* Aarhus University, Denmark

Protein function and folding are perturbed by the presence of interfacial environments. Many protein is active at an interface making it most relevant to study these molecular systems right at the interface. However, the study of the topmost monomolecular layer is made difficult by the high of amount of solvated protein in close proximity to the interesting interfacial species. This calls for spectroscopic methods like sum frequency generation (SFG) spectroscopy, which is inherently surface sensitive from its selection rules and allow studies of the molecularity at the interface based on the vibrational spectrum coming specifically from the interface probing molecular orientation, structure dynamics and interactions. However, extracting this information from the SFG spectrum a challenge due to the non-linear phase sensitive interference affecting the spectrum which can be solved by relating experimental SFG spectra with accurate spectra calculation based on molecular simulation.Wewant to show how information from SFG spectroscopy can be coupled with molecular dynamics simulation to resolvemolecular orientation, dynamics and interactions of proteins at interfaces.

The sum frequency spectrum of the LTα14 peptide shows a characteristic amide I peak at 1640 cm^{-1}signifying the expected α-helical structure, but more specific informationlike interactions with per residueresolution and the nature of their vibrations at the interface is gained bycalculating the SFG spectrum based on state-of-the-art velocity-velocity time correlation functions sampled through molecular dynamics simulation. With this tool we can learn how the frequencies of each individual amino acid residue contributions and inter-residue coupling lead to the inhomogeneous broadening of the surface specific vibrational spectrum. For example, we can learn thatα-helical peptides lying flat on an interface mainly interacts withsurface withthe residues on the side of the helix. The top and bottom positioned residues are more rigid and despitethe bottom residues' close proximity to the surface, they are not as highly perturbed by the presence of the interface.

Furthermore, SFG allowsus to probe the influence of interfacial proteins on the water structure and the vibrational response of interfacial water as the spectra simulations is easily transferred to other molecular systems of interest in the scientific community.

3:00pm SS+AS-MoA-5 Confinement at Solid-solid Interfaces Enhances Crystallinity of COF Thin Films, *Joshua Roys*[1], *J. O'Brien, N. Stucchi,* Clarkson University*; A. Hill,* St. Lawrence University*; J. Ye, R. Brown,* Clarkson University

The condensation reaction of covalent organic frameworks (COFs) on the mica surface demonstrated enhanced crystallinity when physically confined by an exfoliated graphene capping layer. This talk discusses the impact of confinement at a solid-solid interface on two-dimensional COF growth at the solid-solid interface. Understanding confined COF behavior could inform new applications, such as the integration of 2D COFs into 2D van der Waals materials as intercalated layers. The growth of 2D COFs was characterized at the mica-graphene interface by atomic force microscopy (AFM), micro-Fourier transform infrared spectroscopy (micro-FTIR), and density functional theory (DFT). At temperatures sufficient for reaction, AFM topographic and phase imaging observed long-range crystalline growth on the order of square micrometers in graphene-confined domains. Domains outside of the exfoliated graphene flakes did not exhibit long-range mesoscale structural order and retained similar morphology to pre-annealed structures. Micro-FTIR spectra confirmed COF formation both under and outside graphene confinement, as well as an increased presence of trapped water beneath graphene after reactive annealing. Diffusion barriers estimated by DFT calculations suggested the enhanced crystallinity of confined COFs was not the result of heightened mobility of confined molecules or non-covalent self-assembly. The increased COF crystallinity when confined by a graphene layer most likely originated from enhanced

dynamic covalent crystallization due to prolonged exposure to water trapped beneath the graphene flake during the annealing process. This behavior should be universal for condensation-reaction covalent organic frameworks formed under confinement at solid-solid interfaces.

3:20pm SS+AS-MoA-6 Metal Tetraphenylporphyrin Induced Organic/Metal Interactions, *Isheta Majumdar, F. Goto, A. Calloni, M. Finazzi, L. Duò, F. Ciccacci, G. Bussetti,* Politecnico di Milano, Italy

The field of organic electronics has seen the emergence of engineered hybrid metal electrode/organic molecule interfaces where molecules can be ordinally assembled in 2D scalable devices. Metal surfaces can be screened (passivation) by single atomic layers, namely, ultra-thin metal oxide layers, in view of preserving the molecular electronic properties when deposited on the underlying substrate [1].

In the present work, one such system studied is the passivated iron, known as Fe(001)-p(1 × 1)O (preparation protocol in [2]), with a metal tetraphenylporphyrin (MTPP) overlayer deposited under ultra-high vacuum, using a molecular beam epitaxy system. The sample is characterized by ultraviolet photoelectron spectroscopy (UPS) and low energy electron diffraction (LEED). We have observed that transition MTPP (M= Co, Ni, Pt, Pd) deposition on Fe(001)-p(1 × 1)O have resulted in the same *commensurate* (5 × 5)R37° superstructure (37° rotation w.r.t. the main Fe crystal), as observed by LEED pattern. ZnTPP and CdTPP are the only exceptions, which exhibit regular (5 × 5) symmetries, while Fe(Cl)TPP and CuTPP show mixed LEED patterns (presence of overlapping regular and rotated superstructures). This occurrence drove a detailed investigation to find possible strategies (surface engineering) to obtain a specific molecular superstructure.

Therefore, in the next phase of our study, mixed M_1TPP + M_2TPP monolayers were grown sequentially at room temperature by depositing *x* ML of M_1TPP on Fe(001)-p(1 × 1)O followed by (1-*x*) ML of M_2TPP (Fig. 1). The corresponding UPS characterization (Fig. 1 (i)) confirms the monolayer coverages of the mixed MTPP layers. In Fig. 1 (ii), top row: CoTPP (M_1TPP) is deposited first (*x* = 0.25), followed by ZnTPP; bottom row: ZnTPP (M_1TPP) is deposited first (*x* = 0.25), followed by CoTPP. It is observed that the growth of a CoTPP "seed" is able to stabilize a ZnTPP (5 × 5)R37° ordering, not observed on a pure ZnTPP layer. Conversely, a ZnTPP "seed" results in a mixed LEED pattern, where CoTPP molecules retain their characteristic (5 × 5)R37° ordering. This occurrence indicates that there is a significant influence of one type of MTPP over the other that determines the surface reconstruction.

Furthermore, in another set of mixed MTPP depositions, nominally equal amounts of ZnTPP and CoTPP where grown by means of co-deposition on Fe(001)-p(1 × 1)O. In this case, CoTPP showed a certain dominance while influencing the resultant surface reconstruction of the mixed MTPPs. 0.50 ML CoTPP and 0.50 ML ZnTPP co-deposition resulted in a (5 × 5)R37° ordering (Fig. 1 (iii)).

4:40pm SS+AS-MoA-10 Characterization of Oxygen Evolution from Rh(111), *Maxwell Gillum, E. Jamka, C. Grytsyshyn-Giger, F. Lewis, A. Kerr, D. Killelea,* Loyola University Chicago

Due to the importance of oxide surfaces in heterogeneously catalyzed reactions, it is critical to gain a fundamental understanding of the reactivity and behavior of oxygen on these transition metal surfaces. In previous studies we have been able to establish that the reactivity and thermodynamic stability of oxygen on Rh(111) relies in part on the concentration of oxygen present in the subsurface. However, more research needs to be conducted in order to gain a better understanding of the relationship between surface reactivity and subsurface concentration. In addition to the techniques used in our previous studies, namely temperature programmed desorption (TPD) and scanning tunneling microscopy (STM), the experiments herein will include simultaneous infrared (IR)/TPD techniques to gain more information on these critical interactions.

5:00pm SS+AS-MoA-11 Developing a Mechanistic Understanding of Nb$_3$Sn Growth: Sn Adsorption and Diffusion Behavior on (3×1)-O Nb(100), *Rachael Farber,* University of Kansas*; S. Willson,* University of Chicago*; A. Hire, R. Hennig,* University of Florida*; S. Sibener,* University of Chicago

Niobium (Nb) is the current standard material for superconducting radio frequency (SRF) accelerator cavities due to its ultra-low surface resistance and high cavity quality factor (*Q*) at operating temperatures of ~ 2 K. The prohibitively expensive operating and infrastructure costs of these facilities prevent the implementation of accelerator-based technologies across a variety of sectors. Nb$_3$Sn is a promising next-generation material for SRF

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[1] **SSD Morton S. Traum Award Finalist**

cavities due, in part, to an elevated operating temperature of ~ 4.2 K.This significantly reduces the required cryogenic infrastructure and associated operating costs.

Nb_3Sn films are currently grown *via* Sn vapor deposition on preexisting Nb cavities. It is understood that the thickness of the native Nb pentoxide (Nb_2O_5), Sn homogeneity, surface roughness, and alloy thickness must be well controlled for high *Q* film growth.There is not, however, an understanding of the Nb_3Sn growth mechanism resulting in optimal film formation. In this work, we have used a combination of *in situ* ultra-high vacuum (UHV) techniques to visualize Sn adsorption and diffusion behavior on (3×1)-O Nb(100) at the nanometer scale. Scanning tunneling microscopy (STM) data revealed preferential adsorption of Sn along the (3×1)-O unit cell with Sn diffusion guided by the underlying oxide surface as well. Annealing the Sn/Nb(100) sample resulted in the formation of hexagonal and rectangular Sn adlayer structures for all sub-monolayer (sub-ML) and ML Sn coverages studied. Genetic algorithm calculations and DFT based descriptors identified energetically preferred Sn binding sites on the (3×1)-O surface.Calculated STM images corroborated experimentally determined Sn adsorption structures for sub-ML Sn coverages. This spatially resolved, mechanistic information of Sn adsorption and diffusion on an oxidized Nb surface guides the development of predictive Nb_3Sn growth models needed for the further optimization of Nb_3Sn growth procedures.

Author Index

Bold page numbers indicate presenter