

2D Materials

Room A216 - Session 2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA

Surface Chemistry, Functionalization, Bio, Energy and Sensor Applications

Moderator: Mark Edmonds, Monash University, Australia

2:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-1 Molecular Layers on Nanoporous Gold Electrodes, Elizabeth Landis**, College of the Holy Cross
Nanoporous gold presents a surface with high conductivity and surface area, which makes it an interesting platform for surface chemistry. However, the nanoporous gold surface lacks the functionality necessary for many applications including sensing. We have investigated self-assembled thiol-based monolayers and the electroreduction of diazonium-based salts to form aryl molecular layers on nanoporous gold. We use infrared spectroscopy and cyclic voltammetry to show that the molecular layer ordering and density depends on the functionalization method, and the underlying nanoporous surface impacts molecular ordering and electron transfer properties.

2:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-2 Thermotropic Liquid Crystal (5CB) on Two-dimensional Materials, Paul Brown**, American Society for Engineering Education; *S Fischer, J Kofacz, C Spillmann, D Gunlycke*, U.S. Naval Research Laboratory

Current means of redirecting light often rely on either bulky mechanical gimbals or non-mechanical diffractive elements. The former often suffer from wear and are susceptible to failure, while the latter may have significant optical power confined within side lobes. One promising non-mechanical approach that can overcome present limitations in beam redirection incorporates liquid crystal (LC) for continuous, refractive steering. Nematogens, the molecules comprising the LC in a nematic phase, support inherent anisotropic optical and dielectric properties that result from local ordering of single molecules. Recent research suggests the possibility of including two-dimensional materials to act as both an alignment layer and electrode to LC. This offers the possibility of further reducing device dimensions and device response time. Yet little research has focused on the ground state properties of a nematogen interfacing with the two-dimensional substrate. In this talk, we present density functional theory results of the electronic properties of a well-known nematogen (5CB) interacting with graphene, boron nitride, and phosphorene. We also discuss the influence of an introduced single vacancy on the electronic properties of the composite system. We find that 5CB on phosphorene offers the strongest binding of the considered nanosheets. Moreover, we observe qualitatively different band alignments, and focus in particular on type I, which prohibits free carrier transfer between the substrate and nematic LC. Lastly, we discuss the impact of single vacancies on the performance of two-dimensional materials to operate as both an alignment layer and electrode for LC-based applications.

This work has been supported by the Office of Naval Research, directly and through the U.S. Naval Research Laboratory.

3:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-3 Is it Possible to Achieve Intra-molecular Resolution with Ambient AFM?, Vladimir Korolkov**, Oxford Instruments-Asylum Research; *S Chulkov, M Watkins*, University of Lincoln, UK; *P Beton*, The University of Nottingham, UK

Although achieving molecular resolution is now almost a routine across various SPM imaging modes, resolving the actual molecular structure at the atomic level has only been accomplished with NC-AFM in UHV often at low temperatures and with a functionalized probe. Of course, the ultimate goal in SPM is to resolve the chemical structure of a molecule identifying each atom.

In this work we are presenting an approach to achieve intra-molecular resolution on adsorbed molecules in the ambient at room temperatures with a standard AFM cantilever with unmodified tip. We have discovered that using a combination of higher eigenmodes and low oscillation amplitudes (~3-5Å) of a standard Si-cantilever routinely provides ultra-high resolution on adsorbed molecules on surfaces^{1,2} and bulk polymers³.

With this approach we have been able to observe both intra-molecular features and inter-molecular contrast in thin films of coronene and melem molecules on the surface of hexagonal boron nitride (hBN). In case of coronene, all six benzene rings have been resolved as well as underlying atomic lattice of hBN. Unlike coronene, melem forms molecular assemblies with square symmetry stabilized with in-plane strong hydrogen bonds between amino groups. We have observed a strong inter-molecular

contrast where the hydrogen bonds are expected to be. Similar to coronene, the observed intra-molecular contrast was associated with three triazine rings. We have used Probe particle model⁴ to simulate our experimental AFM images and found very good agreement between them. In fact, PPM allowed us a correct interpretation of melem square phase assembly.

Both systems were studied at room and elevated temperatures where we observed phase transitions leading to thermodynamically stable systems. The experimental results are in excellent agreement with density functional theory calculations.

We believe the proposed approach, yet still in its infancy, could potentially provide a pathway to unambiguous identification of molecules on surfaces in the ambient on standard AFM systems.

¹Korolkov et al., Nat. Chem., 2017

²Korolkov et al., Nat. Comm., 2017

³Korolkov et al., Nat. Comm., 2019

⁴Hapala et al., Phys. Rev. B 90, 085421

3:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-4 Tailoring Surface Properties via Functionalized Hydrofluorinated Graphene Compounds, Jangyup Son**, University of Illinois at Urbana-Champaign; *N Buzov*, University of California at Santa Barbara; *S Chen*, University of Illinois at Urbana-Champaign; *D Sung*, Sejong University, Republic of Korea; *H Ryu*, Seoul National University, Republic of Korea; *J Kwon*, Yonsei University, Republic of Korea; *S Kim, J Xu*, University of Illinois at Urbana-Champaign; *S Hong*, Sejong University, Republic of Korea; *W King*, University of Illinois at Urbana-Champaign; *G Lee*, Seoul National University, Republic of Korea; *A van der Zande*, University of Illinois at Urbana-Champaign

Mixing compounds or alloys is an important process to tailor or enhance the intrinsic properties of materials such as chemical reactivity, mechanical strength, and electronic structure. In nanosystems, such as two-dimensional (2D) materials like graphene, transition metal dichalcogenides (TMDCs), and hexagonal boron nitride (hBN), where there is no distinction between the surface and the bulk, mixing of elements is also an important tool for tailoring the interaction of the material with its environment. A successful strategy for manipulating the chemical structures of 2D materials is the chemical functionalization of graphene with single elements such as H, O, N, and F. Yet, an even wider parameter space is possible by combining these functionalization species to produce ternary functionalized graphene compounds.

Here we present a new strategy for producing functionalized graphene compounds through the systematic control of the ratio between adatoms. We demonstrate tailored hydrofluorinated graphene (HFG) compounds via the sequential exposure of graphene to low-energy hydrogen plasma and xenon difluoride (XeF₂) gas. We demonstrate reversible switching of the surface between completely hydrogenated graphene (HG) and fluorinated graphene (FG) as well as the intermediate ratio between two extremes. Moreover, we demonstrate pattern the surface functionalization on a single chip into chemically distinct materials (graphene, FG, HG, and HFG compounds).

Finally, with these patterned structures, we demonstrated tailoring of the surface and electronic properties of the 2D materials. First, the patterned structures enable direct comparisons of the relative surface properties such as wettability and surface friction. Additionally, the electrical properties of functionalized graphene compounds showed unusual recovery of electrical conductance during the partial transformation of FG to HFG, due to initial removal of existing F adatoms when exposed to hydrogen plasma. This study opens a new class of 2D compound materials and innovative chemical patterning that can lead to atomically thin 2D circuits consisting of chemically/electrically modulated regions.

4:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-6 Functionalization of MoS₂ with Halogens, G Copetti**, IF-UFRGS, Brazil; *E Nunes*, IQ-UFRGS, Brazil; *G Soares*, IF-UFRGS, Brazil; *Cláudio Radtke*, IQ-UFRGS, Brazil

Transition metal dichalcogenides (TMDs) with lamellar structures similar to that of graphite have received significant attention because some of them are semiconductors with sizable bandgaps and are naturally abundant. This offers opportunities for fundamental and technological research in a variety of fields including catalysis, energy storage, sensing, and electronic devices. In order to TMDs fulfill their potential, a precise control i) of surface functionalization and ii) of the number of stacked TMD monolayers are mandatory. Surface functionalization was shown to play a key role in

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tuning photoluminescence properties of MoS₂, formation of controllable and low defect density dielectric/MoS₂ interfaces obtained by atomic layer deposition, and etching of MoS₂ layers. Halogenation is one of the most promising functionalization techniques of TMDs. MoS₂ etching with atomic layer control was already achieved by chlorine adsorption associated with Ar⁺ sputtering. Moreover, doping techniques to tune the conductivity and photoemission properties of MoS₂ are essential. Previous works have already shown that incorporation of F-containing species in MoS₂ leads to doping, as well as other interesting properties such as tunable ferromagnetic ordering. In this work, we performed first principal calculations with the density functional theory (DFT) to gain insight into the effect of MoS₂ exposure to halogens. Results evidenced different reactivities while comparing F and Cl, as well as MoS₂ surfaces with variable amounts of defects. These results were explored experimentally. Bulk exfoliated MoS₂ as well as CVD-grown monolayer MoS₂ samples were used. Chlorination was achieved by irradiating the samples with UV light in Cl₂ flux. Prior to chlorination, sputtering of the MoS₂ with Ar ions is performed to induce S removal. X-ray Photoemission Spectroscopy measurements and Rutherford Backscattering Spectrometry showed that S vacancies play a fundamental role in the chlorination process, with vacancy concentration dictating the balance between etching of the MoS₂ layer and Cl incorporation. Fluorination was performed by exposing the samples to pulses of XeF₂. Different degrees of fluorination are achieved by varying exposure time. S is removed and F is incorporated without any loss of Mo. Chemical displacement on the Mo 3d and S 2p XPS peaks was observed after both halogenations processes. These results can clarify the mechanisms of Cl and F incorporation. Finally, the halogenation techniques proposed can be simple and useful methods to adapt the MoS₂ properties for future applications.

4:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-7 Towards Higher Alcohol Synthesis from Syngas on 2D material-based catalysts: A First-Principles Study***, *Tao Jiang, D Le, T Rahman*, University of Central Florida

Synthesis of higher alcohol from syngas has been of great interest owing to the limited petroleum resources and environmental concerns. Rational designing of cheap and efficient catalyst material for such synthesis is in great demand because of diminishing supply of the current state-of-the-art catalysts. Two dimensional (2D) materials are emerging with far-reaching potential for technical and industrial applications thanks to their unique properties, recent developments and improvement of production technologies. In this talk, we will discuss our recent work, based on first principles calculations, towards the unitization of 2D materials as catalysts for higher alcohol synthesis. In particular, defect laden hexagonal boron nitride (*dh*-BN) with N vacancies is excellent catalyst for hydrogenation of CO₂ towards ethanol formation, in the reaction pathway of which the crucial step for forming C₂ bond, i.e. reaction of adsorbed species CH₃* and CO* to form CH₃CO*, is exothermic with reasonably low activation barrier (0.68 eV). On the other hand, we also find single layer of MoS₂ functionalized with small Au nanoparticle to catalyze CO hydrogenation reaction towards ethanol formation. Among all the elementary reactions, the important steps are the reaction of an adsorbed CH₃* and a CO* molecule and the hydrogenation of acetyl to acetaldehyde (both are exothermic with activation barriers of 0.69 and 0.47 eV, respectively) to form C₂ species.[1] The results suggest that 2D materials are suitable candidates for higher alcohol synthesis. Full reaction pathways will be discussed together with results of Kinetic Monte Carlo simulations to shed light on the selectivity of the catalysts. Contact will be made with experimental data that validate our theoretical predictions.

[1] K. Almeida, K. Chagoya, A. Felix, T. Jiang et al, "Towards Higher Alcohol Formation using a single-layer MoS₂ activated Au on Silica: Methanol Carbonylation to Acetaldehyde", submitted

*Work supported in part by DOE Grant DE-FG02-07ER15842

4:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-8 Proton Conductivity Properties of Electrospun Chitosan Nanofibers**, *Woo-Kyung Lee, J Pietron, D Kidwell, J Robinson, C McGann, S Mulvaney*, U.S. Naval Research Laboratory

A major challenge of the 21st century will be to establish meaningful two-way communication between biology and electronics. The study of protonics, devices that mimic electronics but pass protons instead of electrons, seeks to bridge this gap. Protonic conductive materials (PCMs) are essential elements of these devices and we have demonstrated significant improvement in conductivity for chitosan PCMs when deposited as electrospun nanofibers. The observed improvements stem from both enhanced molecular alignment and from chemical doping due to the

electrospinning carrier fluid, trifluoroacetic acid (TFA). We deposited electrospun chitosan nanofibers over palladium protodes and then used the helium ion microscope to isolate single nanofibers for detailed study. We observed that single chitosan nanofibers are strongly doped by TFA with x-ray photoelectron spectroscopy demonstrating extensively protonated nitrogen functionality. With the isolated, single chitosan nanofibers we observed that water uptake, fiber/electrode contact area, and doping concentration are critical parameters of protonic device performance and lead to increased conductivity (*i.e.* low resistivity). The average resistivity of single chitosan nanofibers is $6.2 \times 10^4 \Omega\text{-cm}$, approximately two orders of magnitude lower than the resistivity of cast chitosan PCMs (cast from acetic acid solutions not TFA). We have observed excellent agreement between theoretical models and experiment results that explore each of the contributions to the improved conductivity. In addition, the fabrication and measurement of ionic field-effect transistor of single chitosan fiber using conductive atomic force microscope will be discussed.

5:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-9 Sensor for Breath and Skin Diagnostics**, *Pelagia I Gouma*, The Ohio State University

Resistive gas sensors have received a bad reputation of being largely non-selective.

Our work has produced a crystallo-chemical model for selective gas sensing by polymorphic

metal oxides. The reaction-based and ferro-electric poling sensing mechanisms are discussed

in detail. Novel processing methods to produce the respective nano sensors are presented along

with the device fabrication for the non-invasive diagnosis of gaseous biomarkers in human

and animal breath or skin. This sensor technology is expected to revolutionize medical diagnostics.

5:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-10 Symmetry Controlled Adsorption of Diiodobenzene on MoS₂**, *Zahra Hooshmand*, University of Central Florida; *P Evans, P Dowben*, University of Nebraska - Lincoln; *T Rahman*, University of Central Florida

In a joint experimental and theoretical study, we have uncovered evidence of the importance of symmetry in the adsorption of the isomers of diiodobenzene on MoS₂(0001). The intensity ratio of iodine to molybdenum measured, as a function of exposure for different isomers of the diiodobenzene, show that while for ortho (1,2-) and para (1,4-) diiodobenzene the rate of adsorption at 100 K is very low, that for meta (1,3-) diiodobenzene is considerably more facile. We have applied dispersion corrected density functional theory-based calculations to understand the subtleties in the electronic structure and geometry of adsorption of these diiodobenzene isomers on MoS₂(0001). All three isomers are found to weakly chemisorb with the same binding strength as well as adopt similar configurations. The calculated electron affinity of the three molecules also do not show a specific trend that would verify experimental data. However, analysis of the frontier orbitals indicate that those of 1,3-diiodobenzene are strongly affected by interactions with MoS₂, while that of the other two isomers remain unchanged. Our results show that symmetry is the identifying factor in these adsorption characteristics. The results of frontier orbitals analysis confirm that for adsorption of (1,2-) and (1,4-) diiodobenzene a reduction in the symmetry of the adsorbent is needed. To further validate our conclusions, we compare the above results with that of the adsorption of the diiodobenzene isomers on defect-laden MoS₂(0001).

* Work support in part by DOE grant DE-FG02-07ER15842

5:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-11 Mechanistic Understanding of the CO Hydrogenation Reaction on Defect Engineered 2D-TaS₂ and 2D-MoS₂ Catalysts**, *Mihai Vaida*, University of Central Florida

Due to global energy demands, investigation of catalytic reaction mechanisms on novel catalytic materials that can lead to efficient production of storable fuels from sustainable inputs is of central importance. In this contribution the adsorption of CO and H₂ molecules, as well as the CO hydrogenation reaction are investigated on defect engineered two dimensional (2D) TaS₂ and MoS₂. Crystalline 2D-TaS₂ and 2D-MoS₂ with surface area of 1 cm² are synthesized via a multistep process based physical vapor deposition on Cu(111). The surface composition, morphology, and electronic structure are investigated via Auger electron spectroscopy, low energy electron diffraction, scanning tunneling

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microscopy, scanning tunneling spectroscopy, and photoemission spectroscopy. The interaction of the molecules with the surface and the catalytic reaction mechanisms are investigated via temperature programmed desorption/reaction. No catalytic reactions have been observed on crystalline 2D materials. However, an enhanced catalytic activity is observed after the generation of sulfur vacancies via Ar sputtering. The CO hydrogenation on TaS₂ occurs on low coordinated Ta atoms through the formation of formyl radical (HCO) and formaldehyde (HCOH). On 2D-MoS₂, the CO hydrogenation also occurs on low coordinated Mo atoms. However, in this case the formyl radical splits to form methyldyne radical (CH), which subsequently react with other CH radical to produce acetylene (C₂H₂).

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