

## 2D Materials Focus Topic

### Room 16 - Session 2D+BI+MN+SS-TuA

#### Surface Chemistry, Functionalization, Bio and Sensor Applications

Moderator: Matthias Batzill, University of South Florida

2:20pm **2D+BI+MN+SS-TuA-1 Preserving Chemically Modified Graphene from Thermal and Chemical Loss of Functionality**, *Keith Whitener*, *W Lee*, Naval Research Laboratory; *R Stine*, NOVA Research; *J Robinson*, *D Kidwell*, *C Tamanaha*, *P Sheehan*, Naval Research Laboratory

Chemical functionalization can dramatically alter graphene's properties, enabling one to tune its chemical and physical properties for a wide range of applications. To be useful, these modifications must be stable; however, some of these chemical modifications can be unstable, allowing the material to partially revert to unfunctionalized graphene over time. In this talk, we present our detailed studies of the kinetics of graphene hydrogenation and dehydrogenation. Single layer hydrogenated graphene can be dehydrogenated via thermal, mechanical, and chemical routes. Interestingly, bilayer graphene is much more robust to both chemical and thermal dehydrogenation than is single layer graphene. Possible mechanisms for this difference in reactivity will be discussed. Finally, we leverage the insights from these studies to first fabricate functional chemistries and electronic devices on graphene and then to transfer the devices *in toto* onto arbitrary substrates including biological ones. This enables graphene to act like a chemical "sticky note", transferring chemical and physical properties from one surface to another.

2:40pm **2D+BI+MN+SS-TuA-2 Chemical Vapor Sensing with 1T/2H Phase Engineered MoX<sub>2</sub> Films**, *Adam Friedman*, *A Hanbicki*, *K Perkins*, *G Jernigan*, *J Culbertson*, *P Campbell*, Naval Research Laboratory

Transition metal dichalcogenides (TMDs) show remarkable potential for use in chemical vapor sensor devices. They are inexpensive, inherently flexible, low-power, can be grown in large areas, and have shown high sensitivity and selectivity to electron donor analyte molecules. However, for most devices the conductance response is dominated by Schottky contacts, to the detriment of the sensitivity and obscuring the intrinsic sensing capability of the devices. We use contact engineering to transition the contacts in a MoS<sub>2</sub> FET-based chemical vapor sensor to the 1T conducting phase, leaving the channel in the 2H semiconducting state, thus providing functional Ohmic contacts to the device. We show that the resultant sensors have greatly improved electrical characteristics, are more selective, and recover fully after chemical vapor exposure—all major improvements to previous MoS<sub>2</sub> sensor devices. We study the dynamics of the sensing reactions identifying two possible models for the chemical sensing reaction with physisorption likely dominant. Additionally, we present both conductance and optical evidence that the phase transition can be induced in MoX<sub>2</sub> films by a saturating dose of strong electron donor vapor. We find that the conductance response to strong electron donors in both monolayer MoS<sub>2</sub> and MoSe<sub>2</sub> FET devices ceases after moderate exposure, with final value of the conductance being on order of that expected for the 1T phase. We also examine chemically exposed TMD films intermittently interrogated with Raman and photoluminescence spectroscopy. We observe the appearance of weak characteristic 1T phase Raman features for MoS<sub>2</sub> and we observed a quenching of the photoluminescence of both TMD films that is recoverable with annealing. The data cannot be explained solely by doping mechanisms. Our results suggest a mechanism for a new type of passive chemical vapor sensor.

[1] F.K. Perkins, A.L. Friedman, et al., *Nano Lett.* **13**, 668-673 (2013).

[2] A.L. Friedman, F.K. Perkins, et al., *Sol. St. Elec.* **101**, 2-7 (2014).

[3] A.L. Friedman, F.K. Perkins, et al., *Nanoscale*, **8**, 11445 (2016).

3:00pm **2D+BI+MN+SS-TuA-3 Nanopores in 2D Materials**, *Aleksandra Radenovic*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland  
**INVITED**

Atomically thin nanopore membranes are considered to be a promising approach to achieve single base resolution with the ultimate aim of rapid and cheap DNA sequencing. Recently, we made advances in using nanopore platform for its integration with 2 D materials such as graphene or MoS<sub>2</sub>. Translocation of various types of DNA exhibits a signal amplitude that is five times higher than in the case of solid-state Si<sub>3</sub>N<sub>4</sub> membranes and a SNR of more than 10. These features are highly desirable for event detection and we take advantage of them by showing the electric-field induced unfolding of a 48 kbp long DNA molecule within the nanopore which manifests itself in the quantization of the current drop. Although

single nucleotide identification and DNA sequencing using biological pores have already been demonstrated their fragility, difficulties related to measuring pA-range ionic currents together with their dependence on biochemical reagents, make solid state nanopores an attractive alternative. In this talk I will address novel applications that address identification of single nucleotides but as well go beyond DNA sequencing. We use novel solid state nanopore platform based on atomically thin nanopore membranes in 2D materials such as graphene or molybdenum disulfide for DNA detection, sequencing, water desalination and osmotic power generation.

4:20pm **2D+BI+MN+SS-TuA-7 Spectroscopic Observation of Oxygen Dissociation on Nitrogen-Doped Graphene**, *Mattia Scardamaglia*, University of Mons, Belgium; *T Susi*, University of Vienna, Austria; *C Struzzi*, University of Mons, Belgium; *R Snyders*, University of Mons, Belgium; *G Di Santo*, *L Petaccia*, Elettra-Sincrotrone Trieste, Italy; *C Bittencourt*, University of Mons, Belgium

The reactivity of carbon nanomaterials towards oxygen is very poor, limiting their potential applications as low-cost, high-yield catalysts. However, nitrogen doping is an established way to introduce active sites that facilitate interaction with gases [1,2]. This boosts the materials' reactivity for gas/bio sensing and enhances their catalytic activity for the oxygen reduction reaction, promising to substitute expensive metals in fuel cell cathodes. Despite this interest, the role of differently bonded nitrogen dopants in the interaction with molecular oxygen is obscured by experimental challenges and has so far resisted clear conclusions. We study the interaction of molecular oxygen with graphene doped via nitro-gen plasma by *in situ* high-resolution synchrotron techniques, supported by density functional theory core level simulations [3,4]. The interaction with oxygen gas leads to the dissociation of the molecule and the formation of carbon-oxygen single bonds on the graphene surface, along with a band gap opening and a rounding of the Dirac cone. The change of the N 1s core level signal indicates that graphitic nitrogen is responsible for the observed mechanism: it catalyses the dissociation of an adsorbed oxygen molecule, after which the two O atoms chemisorb with epoxy bonds to the nearest and next-nearest carbon neighbours of the graphitic nitrogen. Our findings help resolve existing controversies and offer compelling new evidence of the ORR pathway.

1. Liu, X., Dai, L. (2016) Carbon-Based Metal-Free Catalysts. *Nat. Rev. Mater.*, **1**, 16064.

2. Ni, S., Li, Z., Yang, J. (2012) Oxygen Molecule Dissociation on Carbon Nanostructures with Different Types of Nitrogen Doping. *Nanoscale*, **4**, 1184-1189.

3. *Scardamaglia, M.* et al., (2016) Tuning Nitrogen Species to Control the Charge Carrier Concentration in Highly Doped Graphene. *2D Mater.*, **3**, 11001.

4. *Scardamaglia, M.* et al., (2017) Spectroscopic observation of oxygen dissociation on nitrogen-doped graphene. Submitted

4:40pm **2D+BI+MN+SS-TuA-8 Back to Black: Can Molecular Networks Preserve the Surface of Black Phosphorus?**, *Vladimir Korolkov*, The University of Nottingham, UK; *I Timokhin*, *R Haubrichs*, CristalTech Sàrl, Switzerland; *S Yang*, *M Schröder*, University of Manchester, UK; *P Beton*, The University of Nottingham, UK

Black phosphorus (BP), one of several allotropic forms of phosphorus, has a layered structure and is a narrow gap semiconductor with a bulk band gap of ~0.3 eV. Similar to other layered materials it can be exfoliated with scotch tape to form a single layer of black phosphorus known as phosphorene. Unlike gapless graphene, phosphorene has a band-gap which was predicted, and later confirmed to be ~2 eV. The band gap is thickness dependent and thus can be easily tuned. Since the first reports of exfoliation of BP, and some 100 years after the first high-pressure synthesis of black phosphorus crystals by Bridgman in 1914, phosphorene or few layered BP has been widely used to construct transistors, including flexible devices.

One of the biggest challenges in BP and phosphorene research remains its stability under atmospheric conditions.

In this work we explore a new route to the solution of this problem through an investigation of the compatibility of BP with the formation of supramolecular networks which have monolayer thickness and are stabilised by non-covalent in-plane interactions, specifically hydrogen bonding. We find that supramolecular networks can be formed on BP and demonstrate this for a mono-component nanoporous array of trimesic acid (TMA) and the bimolecular network formed by cyanuric acid (CA) and

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melamine (M). While the more open TMA array does not passivate the BP surface, the hexagonal melamine cyanurate (CA.M) array is highly effective and provides protection under ambient conditions over a period of more than three months. In addition, we identify the orientation of the CA.M relative to the rows of phosphorus atoms at the surface and, normal to the rows, observe moiré effects which are characteristic of a well-ordered interfacial structure. We have further demonstrated that CA.M monolayers on BP provide a stable platform for the sequential growth of additional molecular layers, for example, 1,2,4,5-tetrakis(4-carboxyphenyl)benzene (TCPB), leading to the formation of a supramolecular heterostructure and demonstrating the facility for further functionalisation of the BP substrate.

Our work demonstrates that a single layer of CA.M can successfully passivate the surface of BP and preserve it intact for at least 3 months. We believe that this facile approach of depositing a passivating organic monolayer stabilised by in-plane non-covalent bonding could be extended to the protection of other two-dimensional materials with air sensitive atomically flat surfaces, and is likely compatible with other solvents and molecules.

The work also presents outstanding examples of high resolution AFM imaging achieved under ambient conditions.

5:00pm **2D+BI+MN+SS-TuA-9 Defect-mediated Properties of Single-layer MoSe<sub>2</sub>**, *Sara Barja*, Materials Physics Center, San Sebastián, Spain; *S Wickenburg*, *Z Liu*, *Y Zhang*, Molecular Foundry, Lawrence Berkeley Lab; *A Pulkkin*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland; *S Refaely-Abramson*, *B Schuler*, Molecular Foundry, Lawrence Berkeley Lab; *H Ryu*, Lawrence Berkeley National Laboratory; *D Qiu*, University of California at Berkeley; *M M. Ugeda*, CIC nanoGUNE, Spain; *Z Shen*, Stanford Institute of Materials and Energy Sciences; *S Mo*, *M Salmeron*, Lawrence Berkeley National Laboratory; *M Crommie*, University of California at Berkeley; *D Ogltree*, Molecular Foundry, Lawrence Berkeley Lab; *O Yazyev*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland; *J Neaton*, *A Weber-Bargioni*, Molecular Foundry, Lawrence Berkeley Lab

**INVITED**  
Properties of two-dimensional transition metal dichalcogenides are highly sensitive to the presence of defects in the crystal structure. A detailed understanding of the defect electronic structure may lead not only to the control of the material's properties through defect engineering towards a particular device application, but also may lead the emergence of novel physico-chemical functionalities. We show how linear mirror twin boundaries and individual atomic defects in single-layer MoSe<sub>2</sub> alter the electronic structure of the pristine semiconductor. Such linear and point defects tend to be highly localized in the plane, which imposes the need of experimental and theoretical characterization of the defects at the atomic level. Using non-contact atomic force microscopy and scanning tunneling spectroscopy, we directly correlate the morphology and electronic properties of structural defects in MoSe<sub>2</sub> at the defect-length scale. We provide direct evidence for the existence of isolated, one-dimensional charge density waves at mirror twin boundaries in single-layer MoSe<sub>2</sub>. We also determine the local density of states of Se vacancies in monolayer MoSe<sub>2</sub> and discuss the correlation to density functional theory calculations, studying the role of the GW approximation to reproduce the energetics of the valence and conduction band as measured in the experimental dI/dV spectra.

5:40pm **2D+BI+MN+SS-TuA-11 Scalable Flexible Graphene Gate TMD Biosensors**, *RamSurya Gona*, *C Naylor*, *C Johnson*, University of Pennsylvania

Two dimensional transition metal dichalcogenides, such as MoS<sub>2</sub> and WS<sub>2</sub>, have been shown to be promising materials for use in bio-sensing. I will present our work on the fabrication of scalable flexible MoS<sub>2</sub> field effect transistors with patterned graphene back-gate. Flexible devices were fabricated on a Kapton substrate and incorporating graphene as the back-gate material due to its biocompatibility and its favorable physical properties. Monolayer MoS<sub>2</sub> single-crystal flakes were grown over large area by chemical vapor deposition, and then transferred onto a pre-patterned electrode array, resulting in a device yield > 70% and an average mobility of 1.0 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. To create nano-biosensors, the surface of the MoS<sub>2</sub> was functionalized via a reengineered mu-opioid receptor and the devices were tested against opioid solutions of various concentrations. This work provides a pathway for the integration of MoS<sub>2</sub> and other TMDs onto flexible/wearable/implantable devices that for trace detection of opioids or

other chemicals. This work was supported by the National Science Foundation through EFRI 2DARE ENG-1542879

6:00pm **2D+BI+MN+SS-TuA-12 Development and Validation of Polarized Models for Peptide-Graphene Interactions**, *Amanda Garley*, University of Colorado Boulder; *N Saikia*, Michigan Technological University; *R Berry*, Air Force Research Laboratory; *H Heinz*, University of Colorado Boulder  
Biosensor technologies require the understanding of interactions between organic and inorganic materials to tune electric response functions, such as peptide assembly on graphitic substrates. Laboratory characterization of specific interactions and molecular assembly can be complemented by atomistic molecular simulations, as well as by quantum-mechanical analysis of band gaps and expected conductivity.

As a first step, we improved common dispersive interatomic potentials for graphite to include pi electron density at virtual sites. The new model reproduces experimental cation-pi energy, X-ray structure, density, cleavage energy, hydration energy, contact angle and elastic constants. As a result we have improved existing models which gave the wrong sign of hydration energies and deviations up to 1000% in these properties from experiment. The parameters are embedded in CHARMM, CVFF, TEAM-AMBER, and other common force fields as part of the INTERFACE force field. An analysis of binding residues, binding energies, conformations, and dynamic information of molecular mobility on the surfaces will be presented.

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