Friday Morning, October 23, 2015

2D Materials Focus Topic
Room: 212C - Session 2D+EM+IS+NS+PS+SP+SS-FrM

Surface Chemistry of 2D Materials: Functionalization, Membranes, Sensors
Moderator: Peter Sutter, University of Nebraska - Lincoln, Judy Cha, Yale University

8:20am **2D+EM+IS+NS+PS+SP+SS-FrM1 Chemically Modifying Graphene for Surface Functionality**, *Paul Sheehan, S. Tsoi, S.C. Hernández, S.G. Walton, T.L. Reinecke, K.E. Whitener, J.T. Robinson*, Naval Research Laboratory, *R. Stine*, Nova Research

Graphene has many superlative properties that may be tailored for specific applications, or even enhanced, through chemical functionalization. Chemical functionalization dramatically changes almost every critical property of graphene, changing it from opaque to transparent, from diamagnetic to ferromagnetic, from electron rich or electron poor, from electrically conducting to insulating (and back again!). This extensive control suggests that chemically modified graphene may aid applications from flexible sensors to surface engineering. I will discuss how stacks of 2D materials can control the dominant surface forces—van der Waals,[1] acid-base interactions, electrostatic interactions, etc.—and so surpass conventional methods of preparing surfaces with, for example, self-assembled monolayers. I will also briefly address goals as diverse as biosensing[2] or sloughing off chemical warfare agents.[3]

[1] ACS Nano, **2014**, *8* (12), pp 12410–12417

[2] BioTechniques, Vol. 57, No. 1, July 2014, pp. 21–30

[3] ACS Nano. 2013 Jun 25;7(6):4746-55.

8:40am **2D+EM+IS+NS+PS+SP+SS-FrM2 Structural Phase Stability Control of Monolayer MoTe₂ with Adsorbed Atoms and Molecules**, *Yao Zhou, E.J. Reed*, Stanford University

Of the Mo- and W- dichalcogenide monolayers, $MoTe_2$ is particularly interesting because it exhibits a small energy difference (approximately 31 meV per $MoTe_2$) between its semiconducting 2H phase and metallic 1T' crystal structures. This feature makes it particularly interesting for potential phase change applications.

We study the adsorption of some common atoms and molecules onto monolayer $MoTe_2$ and the potential for adsorption to induce a phase change between the semiconducting 2H and metallic 1T' crystal structures of the monolayer. Using density functional theory with spin orbit and van der Waals energy contributions, we determined the most energetically favorable adsorption positions and orientations on the two phases of monolayer $MoTe_2$. We then obtained the formation energies for these adsorption reactions and found that atomic adsorption generally favors 1T' metallic phases while molecular adsorption favors semiconducting 2H phases. A possible application of this work may be the chemical stabilization of a preferred phase during the growth process.

Further, we consider the $Mo_xW_{1-x}Te_2$ alloy monolayers that exhibit even smaller energy difference between phases. Our calculations indicate that it may be possible to engineer an alloy ($0<x<0.5$) such that specific molecules will induce a phase change to 1T' while other molecules studied stabilize the 2H phase, which suggests that alloying may provide some molecular selectivity. This potentially provides the basis for molecular sensing applications due to the large electronic contrast between 2H and 1T' phases.

9:00am **2D+EM+IS+NS+PS+SP+SS-FrM3 Selective Nanochemistry on Graphene/Silicon Carbide: Substrate Functionalization and Polycyclic Aromatic Hydrocarbons Formation**, *Patrick Soukiassian*, CEA, France **INVITED**

Graphene & silicon carbide (SiC) are advanced semiconductors having figures of merit scaling well above those of well-established ones [1,2]. Understanding/mediating SiC and graphene surfaces & interfaces properties are of central importance toward functionalization and applications. As a 2D material, graphene is a single atomic layer of carbon atoms in a *sp2* bonding configuration. Therefore, functionalization remains challenging since interacting too strongly with the graphene atomic layer may change its bonding configuration and properties. Instead, interacting with the SiC substrate offers an alternative approach. The 1st case of hydrogen-induced metallization of a semiconductor surface has been shown for a 3C-SiC(001) surface [3]. Here, combining investigations using advanced experimental techniques such as STM/STS, vibrational & 3rd generation synchrotron radiation-based photoelectron spectroscopies together with state-of-art

calculations will be presented and discussed. It includes: i) the 1st evidence of H/D-induced nanotunnel opening at a semiconductor sub-surface shown here for SiC [4]. Depending on H coverage, these nanotunnels could either be metallic or semiconducting. Dangling bonds generated inside the nanotunnels offer a promising template to capture atoms or molecules. These features open nano-tailoring capabilities towards advanced applications in electronics, chemistry, storage, sensors or biotechnology. Understanding & controlling such a mechanism open routes towards selective surface/interface functionalization of epitaxial graphene [4]. ii) The role of H interaction with graphene on SiC dust grains in polycyclic aromatic hydrocarbons (PAH) formation in the interstellar space with a possible route toward prebiotic roots of life in the universe [5].

1–W. Lu, P. Soukiassian, J. Boeckl "*Graphene: fundamentals and functionalities*" **MRS Bull. 37**, 1119 (2012)

2–P. Soukiassian "*Will graphene be the material of the 21th century?*" **MRS Bull. 37**, 1321 (2012)

3-V. Derycke, P. Soukiassian, F. Amy, Y.J Chabal, M. D'angelo, H. Enriquez, M. Silly, "*Nanochemistry at the atomic scale revealed in hydrogen-induced semiconductor surface metallization*", **Nature Mat.2**, 253 (2003)

4–P. Soukiassian, E. Wimmer, E. Celasco, Cl. Giallombardo, S. Bonanni, L. Vattuone, L. Savio, A. Tejeda, M. Silly, M. D'angelo, F. Sirotti, M. Rocca "*Hydrogen-induced nanotunnel opening within semiconductor subsurface*" **Nature Com. 4**, 2800 (2013)

5–P. Merino, M. Švec, J.I. Martinez,P. Jelinek, P. Lacovig, M. Dalmiglio, S. Lizzit, P. Soukiassian, J. Cernichara, J.A. Martin-Gago "*Graphene etching on SiC grains as a path to interstellar PAHs' formation*" **Nature Com. 5**, 3054 (2014)

9:40am **2D+EM+IS+NS+PS+SP+SS-FrM5 Intrinsic Wettability of Graphene**, *Haitao Liu*, Department of Chemistry, University of Pittsburgh

Graphene and graphite are long believed to be hydrophobic. Here we show that a clean graphitic surface is in fact mildly hydrophilic [1]. We find that an as-prepared graphene sample is hydrophilic with a water contact angle of ca. 40°. Upon exposure to ambient air, the water contact angle gradually increased to ca. 60° within 20 min and plateaued at ca. 80° after 1 day. Infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) showed that airborne hydrocarbon adsorbed onto the graphene surface during this process. Both thermal annealing and controlled UV/O_3 treatment removed the hydrocarbon contaminants, which was accompanied by a concurrent decrease in the water contact angle. Our findings show that graphene is more hydrophilic than previously believed and suggest that the reported hydrophobic nature of graphene is due to unintentional hydrocarbon contamination from ambient air.

Reference

[1] Zhiting Li; et al.; Nature Materials, 12, 925-931, (2013)

10:00am **2D+EM+IS+NS+PS+SP+SS-FrM6 Au-doped Graphene As a Promising Electrocatalyst for the Oxygen Reduction Reaction in Hydrogen Fuel Cells: Prediction from First Principles**, *Sergey Stolbov*, University of Central Florida, *M. Alcantara Ortigoza*, Tuskegee University

One of the main obstacles hindering large scale practical application of hydrogen fuel cells is a prohibited cost of the Pt (or Pt-based) catalysts for the oxygen reduction reaction (ORR) on the fuel cell cathode. In this work, we consider Au-doped graphene as an alternative to Pt for facilitating ORR. Our first-principles calculations show that Au atoms incorporated into graphene di-vacancies form a thermodynamically and electrochemically stable structure. Furthermore, calculation of the binding energies of the ORR intermediates reveals that Au-C bonding makes the C atoms neighboring to Au optimally reactive for ORR. The calculated ORR free energy diagrams suggest that the Au-graphene structures have an ORR onset potential as high as that of Pt. We also demonstrate that the linear relation among the binding energy of the reaction intermediates assumed in a number of works on computational high-throughput material screening does not hold, at least for this none purely transition-metal material.

10:20am **2D+EM+IS+NS+PS+SP+SS-FrM7 Spontaneous Deposition of Palladium Nanoparticles on Graphene through Redox Reaction**, *Xiaorui Zhang, W. Ooki, Y.R. Kosaka, T. Kondo, J. Nakamura*, University of Tsukuba, Japan

Due to its unique properties such as huge surface area and excellent conductivity, graphene becomes great interesting for supporting noble metal catalysts. Some noble metals such as palladium, platinum, gold nanoparticles was reported to be able to spontaneous deposition on as-synthesized reduced graphene oxide with external reducing agent-free

recently. Yet the mechanism of spontaneous deposition of metals on graphene has not been clarified until now. In the present research, we spontaneously deposited palladium nanoparticles on as-synthesized reduced graphene oxide in H_2O medium without external reducing agent. It was found that the deposited amount of palladium varied with pH, meanwhile, the bivalent Pd^{2+} precursor was reduced to metallic palladium, and graphene was oxidized simultaneously with an increasing of its oxygen functional groups. The atomic ratio of the deposited Pd and the increased O in rGO located in a range from 1 to 2. As reducing agent-free, the mechanism on spontaneous redox deposition of metal nanoparticles on graphene was proposed, firstly, an efficient adsorption of metal precursor on graphene is a prerequisite which is determined by their electrical charges and adjusted by pH. Secondly, a positive galvanic potential between metal precursor and graphene is necessary for metal spontaneous deposition.

10:40am 2D+EM+IS+NS+PS+SP+SS-FrM8 Gradient Electrochemical Response of Template Synthesized Thickness Sorted MoS$_2$ Nanosheets for Cellular Level Free Radical Detection, *Ankur Gupta*, *T. Selvan, S. Das, S. Seal*, University of Central Florida

The human body is a complex system capable of defending in adverse conditions. A classic example of such complex process is balanced equilibrium production between pro-oxidant and antioxidant in cells. However, when this equilibrium is disturbed, production of free radicals such as superoxide and nitric oxide strengthen, and causes serious cellular damages. Furthermore, myeloperoxidase (MPO) is released during the oxidative burst. This MPO combines with hydrogen peroxide (H_2O_2) and Cl^- and generate hypochlorous acid (HOCl). This is a short-lived and powerful diffusible oxidant strong oxidizer and could react with O^{2-} to produce OH^-. Therefore, in physiological condition HOCl has a major role as a potent microbicidal agent in the immune defense; however, during the oxidative burst HOCl not only damage healthy tissue and generate radicals that are extremely reactive. Therefore, monitoring of the production of free radicals at the cellular level is important for diagnostic purpose. Over past years, several material have been used to develop sensors for free radical detection such as cerium oxide nanoparticles, MoS$_2$ nanosheets and nanoparticles. However, detection of free radicals at cellular level is still a challenge.

In this attempt, layered molybdenum disulfide (MoS$_2$) were synthesized via hydrothermal method. SBA-15 polymer template were utilized during hydrothermal process to grow MoS$_2$ around it to develop porosity. After the hydrothermal synthesis and washing, polymer template was removed by dissolving it in isopropanol which leaves high surface area layered MoS$_2$ crystal. Wet chemical exfoliation of MoS$_2$ were carried out in aqueous solution of Pluronic$^{\text{Ö}}$ F-127 having hydrophobic and hydrophilic chains. Pluronic$^{\text{Ö}}$ F-127 was used to bring down the buoyant density of MoS$_2$. Non-templated nanosheets were synthesized as control. The exfoliated solution were centrifuged at 3000 rpm to remove large particle and supernatant was collected for density gradient ultracentrifugation (DGU). Separation of different thickness layers is carried out by DGU. Thickness sort MoS2 nanosheets were characterized using AFM, XPS, HRTEM, Raman and UV-Vis spectroscopy for structural and chemical analysis. XPS, HETEM and EFTEM analysis of nanosheets have illustrate the sulfur deficiency at the edges of the nanosheets. MoS2 nanosheets were deposited on glassy carbon electrode for cyclic-voltammetry and chronoamperometry measurements. Higher sensitivity and repeatability were demonstrated by nanosheets prepared via template method as compared to control for reactive oxygen and nitrogen species, and HOCl.

11:00am 2D+EM+IS+NS+PS+SP+SS-FrM9 Methanol Synthesis on Defect-Laden Single-Layer MoS$_2$ Supported on Cu(111): Results of a First Principles Study, *D. Le, Takat B. Rawal*, *T.S. Rahman*, University of Central Florida

Despite being found to be the preferred structure in single layer MoS$_2$, the sulfur vacancy row does not facilitate alcohol synthesis from syngas [1] because its narrow size limits adsorption, diffusion, and formation of possible intermediates. On the Cu(111) surface, strong interactions between MoS$_2$ and Cu are expected to reduce the corrugations caused by sulfur vacancy rows, resulting in a larger exposure of vacancies to adsorbates which could enhance the catalytic activity of the row towards alcohol synthesis from syngas. Based on the results of our density functional theory (DFT) simulations utilizing the DFT-D3 correction for accounting the van der Waals interactions, we show that: (1) there is a significant charge transfer from the Cu(111) surface to MoS$_2$, enhancing its catalytic properties, (2) the binding energies of CO and dissociated H_2 increase by 0.3 eV in comparison to that on unsupported MoS$_2$, indicating stronger interactions, and (3) the barriers for forming intermediate species in alcohol synthesis process reduce significantly in comparison to that on unsupported MoS$_2$. On the basis of these energetics, we conclude the Cu(111) substrate promotes methanol synthesis from syn gas on single-layer MoS$_2$ with a vacancy row. We will also present the energetic pathways for the formations of other reaction products such as methane, formaldehyde, and water, as well as that of (the reverse) water gas-shift reaction.

[1] D. Le, T. B. Rawal, and T. S. Rahman, *J. Phys. Chem. C* **118**, 5346 (2014).

11:20am 2D+EM+IS+NS+PS+SP+SS-FrM10 The Happy Marriage of Graphene and Germanium: Graphene Achieves Exceptional Conductivity and Protects Germanium from Oxidizing, *Richard Rojas Delgado*, University of Wisconsin-Madison, *F. Cavallo*, University of New Mexico, *R.M. Jacobberger, J.R. Sanchez Perez, D. Schroeder, M.A. Eriksson, M.S. Arnold, M.G. Lagally*, University of Wisconsin-Madison

The properties of graphene (G) make it an outstanding candidate for electronic-device applications, especially those that require no band gap but a high conductance. The conductance, involving both carrier mobility and carrier concentration, will depend critically on the substrate to which G is transferred. We demonstrate an exceptionally high conductance for G transferred to Ge(001) and provide an understanding of the mechanism.[1] Essential in this understanding is an interfacial chemistry consisting of Ge oxide and suboxide layers that provide the necessary charges to dope the graphene sheet, and whose chemical behavior is such that one can obtain long-term stability in the conductance. In contrast, when high-quality G is grown directly on Ge (100), (111), or (110), the conductance is unexceptional, but oxidation of the surface is significantly delayed and slowed, relative to both clean Ge and Ge with G transferred to its surface . [2,3] We fabricate Hall bars in G transferred to Ge and G grown using atmospheric-pressure CVD with methane precursors . X-ray photoelectron spectroscopy (XPS) is used to investigate the oxide in all stages of the measurements. The sheet resistance and Hall effect are measured from 300K to 10K for transferred and grown samples. Values of mobility and carrier concentration are extracted. It appears we have reached the highest combination of mobility and carrier concentration in graphene (suspended or supported) for temperatures from 10 to 300K. The implication is that the primary mechanisms for scattering charge in the G, roughness and a non-uniform electrostatic potential due to fixed charges, have limited effect when the substrate is oxidized Ge. Finally the subsequent oxidation kinetics of Ge (001) are compared for graphene directly grown on Ge and for graphene transferred to Ge. XPS shows that for graphene grown on Ge(001) the interface is oxide-free and remains so over long periods of time. For graphene transferred to Ge(001) the interface contains stoichiometric and substoichiometric oxides. The thickness of these oxides increases with time, but quite slowly. Using spatially resolved XPS, we propose a model of diffusion limited oxidation initiated at edges of the graphene.

[1]Cavallo, Francesca, et al. "Exceptional Charge Transport Properties of Graphene on Germanium." *ACS nano* 8.10 (2014): 10237-10245.

[2] R. M. Jacobberger, et al. *"Oriented Bottom-Up Growth of Armchair Graphene Nanoribbons on Germanium." Nature Comm.*, under review.

[3] R. Rojas, et. al "Passivation of Ge by Graphene.", in process.

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