

Wednesday Afternoon, November 1, 2017

2D Materials Focus Topic

Room: 15 - Session 2D-WeA

Properties and Characterization of 2D Materials

Moderator: Tien-Ming Chuang, Academia Sinica, Taiwan

2:20pm **2D-WeA1 Multi-scale Mechanics of Graphene Oxide**, *Changhong Cao, M. Daly, C.V. Singh, Y. Sun, T. Filleter*, University of Toronto, Canada

The mechanical behavior of graphene oxide is length scale dependent: orders of magnitude different between the bulk forms and monolayer counterparts. Understanding the underlying mechanisms plays a significant role in their versatile application. A systematic multiscale mechanical study from monolayer to multilayer, including the interactions between layers of GO, can provide fundamental support for material engineering. In this talk, an experimental coupled with simulation approach will be introduced studying the multiscale mechanics of graphene oxide (GO).

GO is a layered nanomaterial comprised of hierarchical units whose characteristic dimension lies between monolayer GO (0.7 nm-1.2 nm) and bulk GO papers ($\geq 1 \mu\text{m}$). Mechanical behaviors of monolayer GO and GO nanosheets (10 nm-100 nm) were comprehensively studied by our group. Monolayer GO was measured to have an average strength of 24.7 GPa, orders of magnitude higher than previously reported values for GO paper and approximately 50% of the 2D intrinsic strength of pristine graphene. The huge discrepancy between the strength of monolayer GO and that of bulk GO paper motivated the study of GO at the intermediate length scale (GO nanosheets). Experimental results showed that GO nanosheets possess high strength in the gigapascal range. Molecular Dynamic simulations showed that the transition in the failure behavior from interplanar fracture to intraplanar fracture was responsible for the huge strength discrepancy between nanometer scale GO and bulk GO papers. Additionally, the interfacial shear strength between GO layers was found to be a key contributing factor to the distinct mechanical behavior among hierarchical units of GO. The understanding of the multiscale mechanics of GO is transferrable in the study of other 2D materials.

2:40pm **2D-WeA2 Modification of Density of States in Iron Chloride Intercalated Epitaxial Graphene with Electric Bias**, *K.D. McAllister, A.P. Sharma*, Clark Atlanta University, *K. Shepperd, E.H. Conrad*, Georgia Institute of Technology, *Michael Williams*, Clark Atlanta University

Epitaxial semi-metallic graphene on the carbon face of silicon carbide has mixed phase AA and AB stacking orders. Iron chloride intercalated graphene is characterized, by contrast, with AA stacking order. The high electronegativity of the iron chloride spacing layers between the graphene bi-layer results in hole-doping of the graphene. Ultraviolet photoemission spectroscopy is used to investigate the electronic structure modifications of stage-1 and stage-3 iron chloride intercalated bi-layer graphene with the application of an external electric field normal to the surface. The dominant features of the study are the modification of the work function and the density of states with the applied electric field and staging order of the intercalant. In particular, the p-type carriers of the stage-1 system are switched to n-type behavior with increasing field strength in agreement with recent models.

3:00pm **2D-WeA3 Anisotropic MoS₂ Nanosheets Grown on Self-Organized Nanopatterned Substrates**, *Francesco Buatier de Mongeot*, *Buatier de Mongeot, Carlo Mennucci*, Università di Genova, Italy, *C. Martella, E. Cinquanta, A. Lamperti*, IMM-CNR, Agrate Brianza (MB), Italy, *E. Cappelluti*, Istituto dei Sistemi Complessi (ISC)-CNR U.O.S. Sapienza Roma, Italy, *A. Molle*, IMM-CNR, Agrate Brianza (MB), Italy

Manipulating the anisotropy in 2D nanosheets is a promising way to tune or trigger functional properties at the nanoscale. Here, a novel approach is presented to introduce a one-directional anisotropy in MoS₂ nanosheets via chemical vapor deposition (CVD) onto rippled patterns prepared on ion-sputtered SiO₂/Si substrates. The optoelectronic properties of MoS₂ are dramatically affected by the rippled MoS₂ morphology both at the macro- and the nanoscale. In particular, strongly anisotropic phonon modes are observed depending on the polarization orientation with respect to the ripple axis. Moreover, the rippled morphology induces localization of strain and charge doping at the nanoscale, thus causing substantial redshifts of the phonon mode frequencies and a topography-dependent modulation of the MoS₂ workfunction, respectively [1].

Additionally the uniaxial morphological modulation of the MoS₂ nanosheets induces a strong dichroism in their optical extinction spectra which is particularly pronounced in correspondence to the C-exciton.

This study paves the way to a controllable tuning of the anisotropy via substrate pattern engineering in CVD-grown 2D nanosheets.

[1] C.Martella et al. Adv. Mater. 2017, 1605785

3:20pm **2D-WeA4 The Potential for Fast van der Waals Computations for Layered Materials using a Lifshitz Model**, *Yao Zhou, L.A. Pellochoud, E.J. Reed*, Stanford University

Computation of the van der Waals (vdW) interactions plays a crucial role in the study of layered materials. The adiabatic-connection fluctuation-dissipation theorem within random phase approximation (ACFDT-RPA) has been empirically reported to be the most accurate of commonly used methods, but it is limited to small systems due to its computational complexity. Without a computationally tractable vdW correction, fictitious strains are often introduced in the study of multilayer heterostructures, which, we find, can change the vdW binding energy by as much as 15%. In this work, we employed for the first time a defined Lifshitz model to provide the vdW potentials for a spectrum of layered materials orders of magnitude faster than the ACFDT-RPA for representative layered material structures. We find that a suitably defined Lifshitz model gives the correlation component of the binding energy to within 8–20% of the ACFDT-RPA calculations for a variety of layered heterostructures. Using this fast Lifshitz model, we studied the vdW binding properties of 210 three-layered heterostructures. Our results demonstrate that the three-body vdW effects are generally small (10% of the binding energy) in layered materials for most cases, and that non-negligible second-nearest neighbor layer interaction and three-body effects are observed for only those cases in which the middle layer is atomically thin (e.g. BN or graphene). We find that there is potential for particular combinations of stacked layers to exhibit repulsive three-body van der Waals effects, although these effects are likely to be much smaller than two-body effects.

4:20pm **2D-WeA7 Tip Enhanced Optical Spectroscopy: A Unique Tool to Address Nanoscale Heterogeneity in 2D Materials**, *Andrey Krayev*, AIST-NT Inc., *M. Chaigneau*, Horiba Scientific, France, *V. Zhizhimontov, A.E. Robinson*, AIST-NT Inc

Raman spectroscopy has proved to be an indispensable tool for characterization of both carbon-based 2D materials, such as graphene or graphene oxide, and TMDCs, providing information on: number of layers, distribution of defects, type of structure and (in case of TMDCs) excitonic behavior. Despite the wealth of the information Raman spectroscopy can provide about the structure of 2D materials, its spatial resolution is limited to approximately 300-500nm, depending on the wavelength of the excitation laser; in many cases this is insufficient for precise characterization of spatial distribution of the variations of structural and the related electronic and optoelectronic properties. Hyperspectral imaging using tip enhanced optical spectroscopy (TEOS), which includes tip enhanced Raman spectroscopy (TERS) and tip enhanced photoluminescence spectroscopy (TEPL), can dramatically improve the spatial resolution of both Raman and PL optical microscopy, providing this much-needed sensitivity.

TERS characterization of graphene and graphene oxide, both pristine and functionalized, reveals a dramatic increase in Raman response at folds and wrinkles in the flakes, as well as over the patterns imprinted in the flakes using an ultrasharp single crystal diamond probe. Interestingly, the wrinkles in graphene oxide flakes exhibit increased conductivity compared to flat areas of the flake, a rather unexpected discovery; as graphene oxide in its normal state is a dielectric, increased thickness of the material might have been expected to result in worse conductivity.

TERS and TEPL analysis of as-grown WS₂ demonstrated significant heterogeneity of the flakes. In an approximately 100nm-wide band adjacent to the flake edges we see both decreased, blue-shifted intensity of the photoluminescence and also increased intensity of the TERS signal; this can be attributed to decreased density of the charge carriers in the vicinity of the edges resulting in increased efficiency of Raman scattering and decreased concentration of trions, which have red-shifted PL relative to regular uncharged excitons.

TERS and correlated surface potential imaging of the WS₂ flakes exfoliated to gold revealed significant nanoscale (from tens to low hundreds of nanometer) variations in intensity of the major Raman bands across the flake. A high resolution map of the photoluminescence distribution extracted from the TERS map of the WS₂ flake clearly delineates that portion of the flake that is single layer. Correlation of the TERS hyperspectral image Raman band intensity with the distribution of surface potential may be diagnostic of TMDC doping level and of the exact sign of the charge carriers.

4:40pm **2D-WeA8 Lithium-Free Covalent Chemical Functionalization of Two-Dimensional Molybdenum Disulfide**, *X.S. Chu, A. Yousef, D.O. Li, A.A. Tang, A. Debnath, D. Ma, A.A. Green*, Arizona State University, *E.J.G. Santos*, Queen's University Belfast, UK, *Qing Hua Wang*, Arizona State University

Two-dimensional transition metal dichalcogenides like molybdenum disulfide (MoS_2) are generating significant excitement due to their unique electronic, chemical, and optical properties. Chemical functionalization is crucial for tuning their properties for use in many applications. Previous methods to covalently functionalize the basal planes of TMDCs require using harsh lithium compounds for intercalation, exfoliation, and phase change from semiconducting to metallic. Here, we demonstrate the direct covalent functionalization of unmodified semiconducting MoS_2 using aryl diazonium salts without lithium treatments. Our approach preserves the structure and semiconducting nature of MoS_2 , results in covalent C-S bonds, and is applicable to MoS_2 derived from mechanical exfoliation, chemical vapour deposition, and liquid phase dispersion. We use density functional theory including van der Waals interactions to determine the reaction mechanism, and support it by scanning probe microscopies. The flexibility of this covalent chemistry is exploited to tether active proteins to MoS_2 , suggesting future biological applications.

5:00pm **2D-WeA9 Spatially Resolved Modification of Graphene's Band Structure by Surface Oxygen Atoms**, *C. Harthcock, A. Jahanbekam, Y. Zhang, David Y. Lee*, Washington State University

We report the spatially resolved modification of the topography and electronic properties of monolayer graphene by low dosage of atomic oxygen in the *nm*-scale. Using an ultra-high vacuum scanning tunneling microscope, we show that surface O-atoms, even at a low coverage of $\text{O/C} \sim 1/150$, form random surface distributions and clusters of various sizes. Using scanning tunneling spectroscopy, oxygen adsorbates are observed to be *p*-type dopants, which leads to site-dependent partial and full band modifications up to a gap of few hundred meV. The degree of band gap opening and the number of O-atom induced charge-holes per area are inversely proportional to the distance between the position at which each STS spectrum is collected and the location of the nearest adsorbate. However, the number of holes contributed per oxygen atom was found to be a site-independent constant of 0.15 ± 0.05 . For a small population of adsorbates taller than 4 \AA , the graphene energy bands are no longer resolved; instead STS measurements show very spatially localized but high density of states over a wide energy range, which indicates sole tunneling contribution from the cluster of electron-rich O-atoms and a complete decoupling from the graphene bands

5:20pm **2D-WeA10 Enabling Atmospheric Pressure Photoelectron Imaging and Spectroscopy using Graphene**, *H.X. Guo*, National Institute of Standards and Technology, *E. Strelcov*, NIST Center for Nanoscale Science and Technology / University of Maryland, *A. Yulaev*, University of Maryland, *Ivan Vlassiuok*, Oak Ridge National Laboratory, *A. Kolmakov*, NIST Center for Nanoscale Science and Technology

We report on recent progress in ambient pressure XPS (APXPS) spectroscopy and electron microscopy of liquid and gaseous samples enabled by electron transparent and molecular impermeable graphene membranes. Single and bilayer graphene membranes are sufficiently transparent to few hundred eV photoelectrons generated by synchrotron or laboratory x-ray sources what makes this experimental platform to be an inexpensive alternative to current differentially pumped APXPS systems. We demonstrate the capabilities of this approach on model liquids and electrochemical cells using a wide array of spectroscopy (AES, XPS, NEXAFS) and imaging (SEM, PEEM) techniques. We also discuss the limitations of this approach and lines of its future development

5:40pm **2D-WeA11 Direct Write Mask Free Fabrication of Semiconductor 2D Architectures on Different Substrates using Aqueous Inks**, *Irma Kuljanishvili, D. Alameri, R. Dong*, Saint Louis University, *L.E. Ocola*, Argonne National Laboratory

Low dimensional semiconductor materials with different sized band-gaps such as 2D atomic crystals, for example WS_2 or MoS_2 layered van der Waals materials, or 1D nanowires (NWs) and nanoribbons such as ZnO, or semiconducting carbon nanotubes (CNTs), have drawn significant attention due to their unique physical, chemical, mechanical properties, and other just to name a few. Low dimensional materials when assembled in vertical or lateral arrangements often lead to the largely enhanced properties, and new functionalities. While the preparation of layered architectures usually involves multi-step fabrication processes it also relies on mask assisted lithographic processes.

Here we present controlled selective preparation of 1D and 2D nanostructures of MoS_2 , WS_2 and ZnO in the variety of geometric assemblies by employing parallel direct write patterning (DWP) of aqueous ink precursors on substrates at predefined locations. In a two-step process (1^{st} patterning and

2^{nd} growth) our unconventional fabrication approach enables simple and flexible production of hetero-structures and other architectures based on "mix and match" principle in precisely controlled fashion. Location specific synthesis of materials also provides access to as-grown interfaces and rapid testing of materials quality, crystallinity and chemical composition which was confirmed by various characterization methods (Raman Spectroscopy, PL, AFM, XRD etc)

Acknowledgement

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6:00pm **2D-WeA12 Band Gap Tuning of MBE Grown WSe_2 via Solution Treatment of Ammonium Sulfide ($\text{NH}_4)_2\text{S}$ and Ozone (O_3)**, *Jun Hong Park*, Institute for Basic Science (IBS), Ewha Womans University, Republic of Korea, *I.J. Kwak*, University of California at San Diego, *A. Rai, S.K. Banerjee*, University of Texas at Austin, *A.C. Kummel*, University of California at San Diego

Transition metal dichalcogenides (TMDs) have been extensively studied because of their unique electronic and optical properties. In addition, having the non-zero band gap, they can be directly integrated in logic devices. However, it is of crucial importance to tune the band gap and Fermi level positions of TMDs effectively to enhance the ON/OFF current ratio. In this study, the band gap of WSe_2 was engineered using a $(\text{NH}_4)_2\text{S}$ solution and a gaseous O_3 treatment. Prior to the chemical treatments, the surface of MBE (molecular beam epitaxy) grown WSe_2 was studied using STM (scanning tunneling microscopy). Large grains of WSe_2 about 100 nm were observed. The band gap of monolayer (ML) WSe_2 was about 2.1 eV in STS (scanning tunneling spectroscopy), consistent with previous STM studies. A bare WSe_2 sample was emerged in ammonium sulfide solution (40% $(\text{NH}_4)_2\text{S}(\text{aq})$) at 300K. Afterward, the sulfur treated (ST) WSe_2 sample was transferred to a UHV scanning tunneling microscopy (STM) chamber to observe the effect of the treatment on the band gap. The STM imaging revealed that new electronic states were generated by ST across the entire WSe_2 surface, with asymmetric bias dependence. In STS, band gap of the ST WSe_2 was reduced to 1.2 eV, while Fermi level was pinned near the valence band. A WSe_2 field effect transistor (FET) was fabricated to show the effect of ST on electrical properties. Electrical measurement showed that ST of monolayer WSe_2 transistors increased ON states current by two order of magnitude in the *p*-branch, while ON state current in *n* -branch was increased by an order of magnitude which is consistent with the $(\text{NH}_4)_2\text{S}$ decreasing the band gap and inducing *p*-type doping. The band gap was also tuned by ozone (O_3) treatment at room temperature. A MBE grown WSe_2 was inserted in a vacuum chamber. O_3 gas was prepared by UV lamp excitation of a continuous O_2 flow into the chamber at 300 K for 2 min. After dosing O_3 gas for 2 min, the band gap of the WSe_2 was about 1.3 eV, while Fermi level was near conduction band indication (*n*-type). As exposure time of O_3 increased to 6 min, the band gap of ML WSe_2 was decreased to 1.1eV and the formation of WO_x was observed on the ML terraces. Therefore, O_3 had the opposite behavior of $(\text{NH}_4)_2\text{S}$ since O_3 treatment maintained *n*-type doping while shrinking the band gap.

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