

2D Materials Technical Group

Room 303 - Session 2D+AS+BI+HC+SS-FrM

2D Materials: Biological, Electronic, Energy, and Other Applications

Moderators: Robert Hovden, University of Michigan, Jyoti Katoch, Carnegie Mellon University

8:20am 2D+AS+BI+HC+SS-FrM-1 Printable Electrochemical Biosensors based on 2D and 3D Graphene, A. Ebrahimi, Derrick Butler, V. Kammarchedu, K. Zhou, Penn State University

INVITED

The increasing demand for low-cost and field-deployable biosensors has driven researchers to explore robust and scalable biochemical sensor materials and fabrication strategies. Compared to more complicated and expensive photolithography methods, printing techniques – including inkjet and direct laser writing – can enable tailorable and easily-prototypable sensors that are conducive to testing at the point of need. Electrochemical sensors have the potential to meet these criteria and integrate well with printing methods.^[1] In recent years, graphene has emerged as a key material in the area of electrochemical biosensors due to high conductivity, wide electrochemical window, biocompatibility, tunability, and excellent surface sensitivity.^[2] In particular, advances in preparation of solution-phase graphene suspensions (such as inks containing 2D graphene sheets) have brought about breakthroughs in printed electronics, while the advent of laser-induced graphene (LIG) has enabled the direct writing and integration of 3D porous graphene patterns in various low-cost substrates. Over the past few years, our group has developed different facile functionalization methods to enhance the sensitivity and specificity of printed devices based on graphene ink and LIG, with special attention to sensor performance in complex biological fluids (such as serum, saliva, sweat).^[3,4] We have investigated application of the sensors for *in vitro* detection of small molecules involved in neurological functions, kidney disease, and wound infection as well as real-time monitoring of drug-induced response of cancer cells and biofilm biomarkers. Interfacing of the printed sensors with low-cost readout electronics and smartphone has been also demonstrated to showcase the sensor applicability for remote sensing at the point of need. Convergence of machine learning with electrochemical sensing has been also investigated, demonstrating a significant enhancement of sensitivity, while enabling reliable multiplexing of example biochemical markers in saliva and sweat. This talk will highlight our recent progress and ongoing work on advancing printable graphene biosensors in more detail.

[1] K. Yamanaka, M. C. Vestergaard, E. Tamiya, *Sensors (Switzerland)* **2016**, *16*, 1761.

[2] A. Bolotsky, D. Butler, C. Dong, K. Gerace, N. R. Glavin, C. Muratore, J. A. Robinson, A. Ebrahimi, *ACS Nano* **2019**, *13*, 9781.

[3] R. Muralidharan, V. Chandrashekar, D. Butler, A. Ebrahimi, *IEEE Sens. J.* **2020**, *20*, 13204.

[4] D. Butler, D. Moore, N. R. Glavin, J. A. Robinson, A. Ebrahimi, *ACS Appl. Mater. Interfaces* **2021**, *13*, 11185.

9:00am 2D+AS+BI+HC+SS-FrM-3 A Large Area Selective Emitter for Thermophotovoltaic Applications, Minsu Oh, K. Grossklaus, D. DeMeo, Z. Kranefeld, T. Vandervelde, Tufts University

Thermophotovoltaic (TPV) devices enable energy harvesting from waste heat. In a TPV system, photons radiated by a selective emitter are converted into electricity by a photodiode due to the photovoltaic effect. The total photon flux available for power conversion is determined by the temperature, emission spectrum, and size of the emitter. Due to the engineerability of metamaterial's optical properties, they have been widely used to create TPV emitters with a desired emission spectrum for varying heat source temperatures. However, the difficulties in fabricating nano- or micrometer-sized metamaterial features that are two-dimensional over large areas pose challenges to realizing a large emitter. This fundamentally limits the output power of a TPV system due to power density restrictions. Therefore, achieving large area emitters with engineerable optical properties are critical for utility of TPV devices at scale with a reasonable power output. In this work, we experimentally demonstrate a 4-inch diameter selective emitter fabricated from one-dimensionally patterned Si and Cr. The selective emission of the emitter peaks at 3.75 μm , which targets 773K blackbody temperature, with a bandwidth of less than 1.5 μm . The emission bands of this structure can also be engineered for varying source temperatures owing to the interference effects. Moreover, due to the fabrication ease, our emitter can easily be scaled up to any size of the

substrate. We also present the impact of temperature and oxidation on the emission band when heated up to 1000K.

9:20am 2D+AS+BI+HC+SS-FrM-4 Advanced Two-Dimensional Nanohybrids for Efficient Electrocatalytic Hydrogen Evolution, Fei Yao, University at Buffalo-SUNY

Hydrogen (H_2) shows great potential in reducing greenhouse gas emissions due to its environmentally friendly nature and high gravimetric energy density. It can be generated via electrochemical water splitting based on the hydrogen evolution reaction (HER). It is well known that Pt-group metals (PGMs) are excellent catalysts for HER, but their broad adoption is limited by high cost and scarcity. Recently, two-dimensional (2D) molybdenum disulfide (MoS_2) is regarded as a promising alternative to PGMs due to its large surface area, rich active sites, and ideal hydrogen adsorption energy. However, its practical application is hindered by the intrinsically low electrical conductivity arising from the semiconducting nature of 2H phase MoS_2 . On the other hand, 2D Ti_3C_2 MXene with high electrical conductivity, excellent hydrophilicity, and large interlayer distance has been intensively investigated in energy storage devices lately. Compared with charge-neutral graphene, MXene exhibits a negatively charged surface due to the existence of numerous surface functional groups (-OH, -O, -F, etc.), which not only enhances the dispersion of MoS_2 precursors but also promotes MoS_2 nucleation, making it a superior template for MoS_2 synthesis. Nevertheless, undesired oxidation of MXene occurs in aqueous solutions, reducing the overall catalyst stability.

To address the above issues, we employed a one-step solvothermal method using DI water/DMF as bisolvent and constructed a metallic 1T phase-enriched $\text{MoS}_2/\text{MXene}/\text{CNT}$ composite as HER catalyst. A low overpotential (169 mV) and Tafel slope (51 mV/dec) along with the highest turnover frequency (7 s^{-1} at -0.23V vs. RHE) and an ultralong lifetime (72 hours) was successfully achieved. The origin of the outstanding HER performance of the ternary composite can be ascribed to: (i) the prevention of 2D layer restacking as well as the enlarged surface area due to the 2D/2D $\text{MoS}_2/\text{MXene}$ integration and ion intercalation; (ii) the vertical growth of MoS_2 flakes on the MXene template which increases the exposure of MoS_2 edge planes, maximizing the total number of active sites; (iii) the synergistically enhanced conductivity because of the formation of hybrid 1D/2D conductive network via the integration of 1T-phase metallic MoS_2 , conductive MXene backbone with suppressed oxidation along with the CNT crosslinks, minimizing the charge transfer resistance at the electrode/electrolyte interface. This work demonstrated an effective strategy for two-dimensional material structure-property engineering with the aim of optimizing the HER performance which will shed light on the development of the next-generation PGM-free HER electrocatalysts.

9:40am 2D+AS+BI+HC+SS-FrM-5 Bandstructure Engineering in Two-Dimensional Semiconductors, Keun Su Kim, Yonsei University, Republic of Korea

INVITED

The tunable band structure of two-dimensional quantum matter is not only interesting in itself, but also useful for the fundamental study of condensed matter physics. As example, surface chemical doping can be used to reduce the band gap of black phosphorus over the energy range greater than its intrinsic band gap [1]. This could be used to deliberately induce a topological phase transition to a Dirac semimetal phase protected by spacetime inversion symmetry [2]. It could also be used to trace the evolution of quantum phases (pseudospin) order across the topological phase transition [3]. In this talk, I will introduce our recent study on the band renormalizations and pseudogap of black phosphorus doped by alkali metals [4]. Using angle-resolved photoemission spectroscopy (ARPES), we found that the simple quadratic band dispersion of doped black phosphorus anomalously bends back towards zero wavenumber, which can be explained by Anderson-McMillan's framework developed for the band structure of liquid (or disordered) metals in the 1960s. This is a natural consequence of resonance scattering by the potential of dopant ions with short-range order. The depth of scattering potential tuned by different kinds of alkali metal (Na, K, Rb, and Cs) allows us to classify the pseudogap of p-wave and d-wave resonance.

1. J. Kim et al., *Science* **349**, 723 (2015).
2. J. Kim et al., *Phys. Rev. Lett.* **119**, 226801 (2017).
3. S. W. Jung, S. H. Ryu et al., *Nature Mater.* **19**, 277 (2020).
4. S. H. Ryu, M. Huh, D. Y. Park et al., *Nature* **596**, 68 (2021).

Friday Morning, November 11, 2022

10:20am **2D+AS+BI+HC+SS-FrM-7 Graphene – Ferritin Interface Unpins Fermi-Level and Induces Temperature Dependent Coherent Tunneling Across Biomolecular Junctions, Ayelet Vilan**, Weizmann Institute of Science, Israel; *N. Kumar Gupta*, National University of Singapore; *S. Kumar Karuppannan*, National Quantum Fabless Foundry, Singapore; *R. Reddy Pasula*, Nanyang Technological University Singapore; *J. Martin, W. Xu*, National University of Singapore; *E. May*, Nanyang Technological University, Singapore; *A. Pike*, Newcastle University, UK; *H. Astier, T. Salim*, National University of Singapore; *S. Lim*, Nanyang Technological University, Singapore; *C. Nijhuis*, University of Twente, Netherlands

Molecular electronics is one road to ultimate miniaturization: can we reduce the size of an electronic element to a size of a single molecule? However, as the size reduces to few-atoms level, it becomes harder to distinguish the role of the molecular core from that of the contacts. Here we show the prominent role of graphene interfaces with Fe storing proteins in the net charge transport across their tunnel junctions. Here, ferritin (Afftn-AA) is adsorbed on graphene by non-covalent amine-graphene interactions. In contrast to junctions with metal electrodes, graphene has a vanishing density of states toward its intrinsic Fermi-level (“Dirac point”), which increase away from the Fermi-level. Therefore, the amount of charge carriers is highly sensitive to temperature and electrostatic charging (induced doping), as deduced from a detailed analysis of charge transport as a function of temperature. Moreover, increasing the iron loading of ferritin, changes the graphene from n- to p-doping. Remarkably, the temperature dependence can be fully explained within the coherent tunneling regime due to excitation of hot carriers. The sensitivity of graphene (and 2D materials in general) to electrostatic charging opens rich possibilities in employing interface electrostatics in tuning the electronic properties of molecular junctions and is important for 2D / biomolecules hybrids in general.

10:40am **2D+AS+BI+HC+SS-FrM-8 The Influence of Selenium Incorporation on the HER Catalytic Activity of Electrodeposited Se-MoS_x Electrocatalysts, Lee Kendall, G. Zangari, S. Mc**, University of Virginia

With the increase in the global consumption of energy, the need to meet the growing energy demands has put significant pressure on the current means of energy production and storage. To meet this demand, water splitting has seen substantial efforts in developing catalytically active materials that replace costly materials, such as Pt, to allow for economically viable implementations. MoS₂ has attracted significant attention over the past decade due to its low cost and availability. Additionally, MoS₂ is one of the most promising materials for electrocatalytic hydrogen evolution as its Gibbs free energy of hydrogen adsorption, $\Delta G_{\text{H}_2, \text{ads}}^{\text{H}}$, is the closest to Pt, a state-of-the-art catalyst, when compared to other metallic materials. However, due to the limited number of accessible edge sites, as well as high kinetic barriers for H₂ evolution, the catalytic performance of MoS₂ is still far from the needed requirements. To address this, researchers have investigated amorphous MoS_x due to its increased structural heterogeneity that increases catalytic site density. Combined with short-range atomic arrangements that enable adequate electronic conductivity, amorphous MoS_x is an attractive candidate for electrochemical processes. This can be further improved, however, as the bridging bonds are the most catalytically active while the terminal and apical are significantly less active. To increase their activity, we investigated incorporating selenium into MoS_x due to the success in crystalline, selenium alloyed MoS₂. This success centered on obtaining a more thermoneutral $\Delta G_{\text{ads}}^{\text{H}}$ for the sulfur edges and basal plane, similar motif to terminal and apical bonds in the amorphous system, respectively. To accomplish this, we used an electrodeposition technique that allows for the incorporation of selenium into the MoS_x polymeric chains. We will report on this investigation of the electrodeposition of Se-MoS_x and its effect on the physical, electronic, and catalytic properties towards the hydrogen evolution reaction. Through electrodepositing catalytically active Se-MoS_x thin films, this effort demonstrates improved HER efficiency over current, low-cost materials.

11:00am **2D+AS+BI+HC+SS-FrM-9 Two-Dimensional Skintronics, Dmitry Kireev, D. Akinwande**, The University of Texas at Austin **INVITED**

Modern healthcare displays a significant shift from hospital-based medicine towards a personalized, ambulatory, and wearable approach. In this regard, the development of skin-wearable electronics (*skintronics*) is an essential step toward mobile health monitoring, the healthcare Internet of Things, and eventually preventive medicine. Continuous long-term monitoring of brain activity, heart activity, body hydration, or temperature, is vital for better comprehension of human physiology, understanding systematic disease risk factors, and building preventative care solutions. In this work, we utilize *graphene* and other *2D materials* such as platinum

diselenide (PtSe₂) and platinum ditelluride (PtTe₂) to construct the thinnest elements of skintronics - electronic tattoos. The PtSe₂ and PtTe₂ e-tattoos that can be grown at comparably low temperatures (400°C) were found to have superior sheet resistance and electrode-skin impedance compared to monolayer graphene e-tattoos. On the other hand, we also report on the significant advancement of the classic graphene electronic tattoos by introducing graphene nanoscrolls and stacking multiple graphene monolayers. Moreover, we show that graphene tattoos can be made unsusceptible to sweat by introducing microholes into their structure. Significantly, we show that graphene electronics tattoos can be used for deep tissue monitoring, detecting complex analytes such as blood pressure and respiration rate in a continuous and entirely non-invasive manner. Beyond the simple use of graphene tattoos as passive electronic elements, we have discovered that the semimetallic 2D material can be used as transistors, biased electrostatically through the body itself, creating transistor tattoos. The body-gated graphene tattoo transistors can function as biosensors or small-signal amplifiers, contributing to the development of higher-fidelity electrophysiology measurements and decreased susceptibility to movement-related artifacts.

11:40am **2D+AS+BI+HC+SS-FrM-11 Ultrasonic-Assisted Assembly of Metal Nanoparticles within Graphene Oxide for Tailoring Stem Cell Response, J. Jaiswal**, Indian Institute of Technology (Banaras Hindu University), India; **Marshal Dhayal**, Indian Institute of Technology (Banaras Hindu University), India

Recently 2D material-assisted stimulation for cellular functions has gained significant attention. In this paper, we will be presenting the methodology used for preparing tunable properties of 2D surfaces incorporating metal nanoparticles (NP) within graphene oxide sheets. The study will report the use of mechanical forces generated through an ultrasonication-assisted method for increased diffusion of metal ions in graphene oxide (GO). The transmission electron microscopy (TEM) analysis has been used to confirm the distribution of metal particles in GO sheets whereas Raman spectra were used to identify the relative changes in the Raman bands. The study presents a correlation of these observations with corresponding confirmation in the distortion of multilayer assembly of thin layers of GO by the nucleation of metal nanoparticles. The X-ray diffraction (XRD) spectra of GO-NP also demonstrated similar outcomes in Raman spectra. UV-visible spectra and X-ray photoelectron spectroscopy (XPS) analysis were used to determine optical activity and relatively % proportions of their atomic concentrations. These unique combinations of functionally graded GO-NP were used to study the response of human mesenchymal stem cells. This method may be helpful to address the challenges associated with developing metallic assembly within graphene oxide without chemical functionalization of their inert surface for their application in the biomedical field.

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