Two-Dimensional Layered Materials (MoS_2/Graphene As Nanocatalysts for Hydrogen Production

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Abstract Synopsis (Part I)

Graphene and related nanomaterials are attracting a great deal of attention as potential game changer at the grand challenge of energy-water sustainable technologies. The related applications require delicate control over geometric and electronic structures affecting physical and electrochemical properties. In this study, we prepared a range of three-dimensional graphene-based aerogels with varying graphene oxide-MoS_2 (molybdenum disulfide) composition under hydrothermal conditions (P < 20 bar, T < 200 °C). We demonstrate that precise control of defects density (via MoS_2 desulfurization), hierarchical porosity and topological interconnectedness (via monolithic aerogels), invoked in synthesized reduced graphene oxide-MoS_2 aerogels that can finely tune morphology, structure, and enhance heterogeneous electron transfer rate (k_{ET}). This study allowed to design graphene heterostructure interfaces, understand their interaction through optical absorption and Raman spectroscopy (RS), to correlate between number defect density (via RS) and heterogeneous electron transfer rate (via scanning electrochemical microscopy; SECM) quantitatively, useful for fuel cell applications. Additionally, Raman spectral bands are analyzed in terms of band position, intensity and integrated intensity ratio determining structural disorder, inter defect distance, number defect density, interaction and number of MoS_2 layers. Moreover, the pore size distribution and mesoporosity are determined from electron microscopy and tomography. The multiple roles of oxygenated (carbonyl; C=O, carboxyl; -COOH) surface functionalities in graphene and MoS_2 and bonding configurations are emphasized for improved physicochemical properties.

Abstract Synopsis (Part II)

Recent development of two-dimensional layered materials including graphene-family and related nanomaterials have arisen as potential game changer for energy, water and sensing applications. While graphene is a form of carbon arranged hexagonally within atomic thin sheet, MoS_2 is becoming a popular, efficient, and cost-effective catalyst for electrochemical energy devices, in contrast to expensive platinum and palladium catalysts. In this work, we electrochemically desulfurize few-layer molybdenum disulfide (MoS_2) and aerogels with reduced graphene oxide (rGO) prepared hydrothermally, for improving hydrogen evolution reaction (HER) activity via point defects (***S-vacancy***). Moreover, the interactions between rGO and MoS_2 components create emergent heterostructures with desirable physicochemical properties (specific surface area, mechanical strength, faster diffusion, facile electron and ion transport) enabled by chemically bridged (covalently) tailored interfaces. We demonstrate that with an optimized number defect density, particularly by exposing the edges of MoS_2 layers and nanowalls in graphene-MoS2 'hybrid' aerogels, interfacial processes during catalytic reactions are accelerated. To understand the effects of defects on HER activity, we varied the applied potential and operating duration for optimized defect density. This study offers a unique method for tuning the properties of layered MoS_2 and hybrids as promising, cost-effective and efficient nanocatalysts and establishes the structure–catalytic activity relationships via scanning electrochemical microscopy (SECM) at electrode/electrolyte interface besides mapping electrochemical (re)activity and electro-active site distribution.

(PART I) Synthesis and Characterization of Mesoporous Reduced Graphene Oxide/MoS_2 'hybrid' Composites.

Background: Graphene, atom-thick two-dimensional crystalline allotrope of carbon atoms arranged in a honeycomb or chicken wire mesh like pattern, has stimulated extensive interests. Additionally, the emerging two-dimensional (2D) materials exhibit a wide range of electronic properties, ranging from insulating hexagonal boron nitride (h-BN), semiconducting transition metal di-chalcogenides (TMDCs) such as molybdenum disulfide (MoS_2) and tungsten di-selenide (WSe_2), to semi-metallic graphene. Graphene, an atomic thin sheet of sp^2-hybridized carbons joined covalently to form a two-dimensional hexagonal honeycomb lattice, has stimulated extensive research and development interests. The plethora of 2D materials together with their hetero-interfaces, which are free of the traditional "lattice mismatch" issue, brings new opportunities for exploring novel electrical, electrochemical and photonic phenomena. In this study, we design graphene-MoS_2 hybrids to enhance their interactions with electrolyte through their intrinsic and extraordinary physical-chemical properties, electrochemical activity and large specific surface area. Finally, the relatively large-bandgap layered material, MoS_2, bridges the zero gap graphene. The combination of these materials and the approaches for enhancing interactions offers the promise of scientific discoveries and novel electrochemical technologies including renewable energy sources and enhanced hydrogen evolution reaction for fuel cell applications.

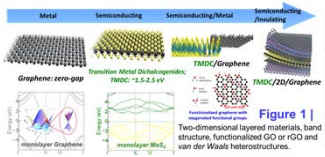


Figure 1 | Two-dimensional layered materials, band structure, functionalized GO or rGO and *van der Waals* heterostructures.

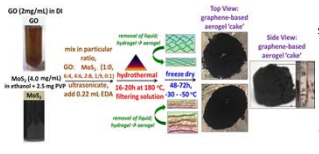


Figure 2 | Schematic of hydrothermal synthesis and three-dimensional network of graphene and MoS_2 with hierarchical mesoporosity and topological interconnectedness. *Gupta, Meek, Evans, Dimakis, J. Appl. Phys.* ***124***, *124304 (2018).*

Liu, Y. et. al. (2016) *Mat. Res. Meter.* doi:10.1038/natrevmats.2016.42

Results Electron microscopy revealed surface morphology, internal microstructure, and electron diffraction of all the aerogels. XRD provided crystal structure and effects of rGO on MoS_2. Raman spectra showed characteristic first-order D (disorder-activated) and G (graphitic or sp^2 C) bands and second-order 2D (intrinsic to sp^2 C), besides MoS_2 related bands. The Raman spectral analysis is carried out for various metrics and plotted. By employing UV-Vis absorption and photoluminescence emission spectroscopy we obtained electronic structure and bandgap.

Figure 3 | Electron Microscopy and Electron Diffraction Properties

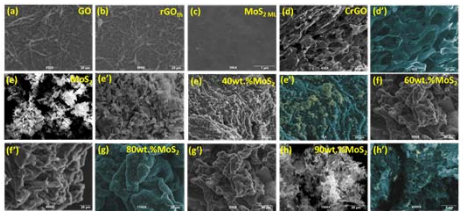
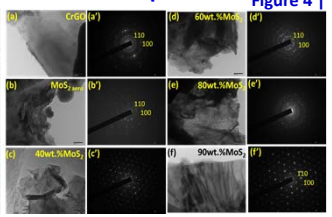


Figure 4 |



X-ray Diffraction, Raman Spectroscopy, UV-Vis Absorption and Photoluminescence Spectroscopy

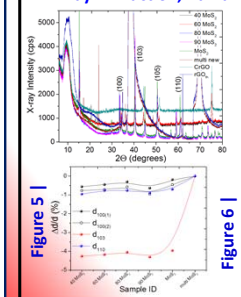
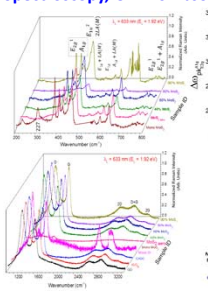


Figure 5 |

Figure 6 |



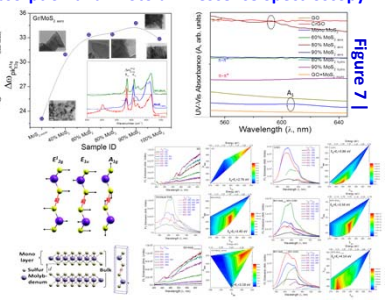


Figure 7 |

Summary 1. SEM and TEM elucidate surface morphology of graphene-family nanomaterials (GFNs) including CrGO and Gr-MoS_2 with varying MoS_2 ratio aerogels. The oxygenated functionalities modify graphene nanosheets while displaying mesoporosity. The graphene nanosheets with MoS_2 create multiplexed tailored interfaces crucial for applied electrochemical applications. 2. Optical spectroscopy, particularly PLE show variation in the position of emission band with excitation wavelength implies presence of midgap states in the vicinity of graphene Dirac cone and tunable bandgap with MoS_2 as anticipated. 3. Raman spectral analysis in terms of difference in position of two bands related MoS_2 showed presence of multilayered MoS_2 architecture. 4. Various functionalized and mesoporous nanosheets of two-dimensional layered materials reinforce density of states resulting in tunable density of states. 5. Combination of Raman spectroscopy and Raman mapping and results from advanced electrochemistry (*i.e.* SECM) help to establish *structure-activity relationships* for a range of graphene-MoS_2 nanoporous materials in this study (**see Part 2**). $$$ KY NSF RSP (T.R.) and KY NASA UF (J.D.) funding are acknowledged.

(PART 2) Electrochemical Desulfurization of Molybdenum Disulfide (MoS_2) As Nanocatalysts Supported on Reduced Graphene Oxide for Hydrogen Evolution.

Background: Intense research activity on alternative energy sources is stimulated by continuously increasing global demand on electrical energy in 21st Century digital electronics age. The electrochemical energy conversion & storage systems represent efficient and environmentally benign technologies. Owing to their unique power and energy density range which fills the gap between traditional capacitors and batteries namely, supercapacitors and electrocatalytic fuel cell play a vital role. Therefore, the development of functional nanoelectrode materials with greater noble-metal free catalytic performance becomes indispensable. Hybrid nanomaterials creating tailored hetero-interfaces by utilizing variants of graphene i.e. graphene oxide (GO) and reduced GO coupled with molybdenum disulfide (MoS_2) with point defects (known as S-vacancy), introduced via electrochemical desulfurization, as high-performance noble-metal free electrodes are proposed. Here in this study, we demonstrate the continuous tuning of layer vertically aligned MoS_2 aerogels with graphene or supported on reduced graphene oxide. Moreover, we show the significant improvement of the hydrogen evolution reaction activity. A strong correlation between such tunable material properties and hydrogen evolution reaction activity will be established. This work will provide an intriguing and effective approach on tuning electronic structures and properties for augmenting the electrocatalytic activity for fuel cells.

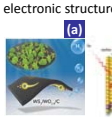


Figure 1 [HER and S-Vacancy] | (a) HER activity on dichalcogenides loaded graphene support. (b) HER activity of monolayer MoS_2. (c) Theoretical predictions (*Tsai et al. Nat. Commun.* **8**, 15113 (2017); *DOI:10.1038/ncomms15113*). (d) Graphene-MoS_2 *van der Waals* hetero-interfaces.

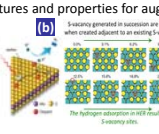


Figure 2a (Electrochemistry) | Schematic of traditional electrochemistry set-up (macroelectrode geometry).

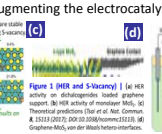
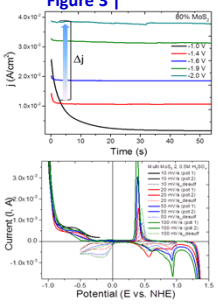


Figure 2b (SECM) | Schematic of SECM set-up (microelectrode geometry).

Results The electrochemical desulfurization, cyclic voltammetry, linear sweep voltammetry and scanning electrochemical microscopy studies are performed and shown below demonstrating pseudo-capacitive behavior and over-potential.

Electrochemical Properties and Desulfurization

Figure 3 |



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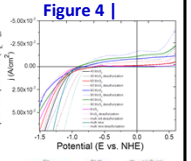
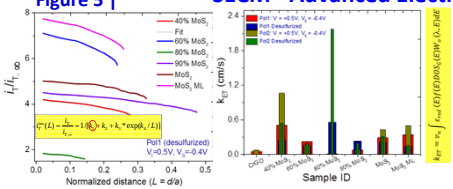
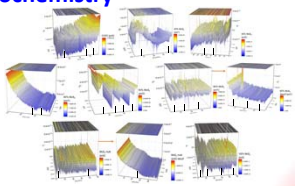


Current density (j) with increasing negative potential increases in the magnitude indicative of vacancy creation.

$$I_{ss} = (2.69*10^5)n^{3/2}ACD^{1/2}v^{1/2}$$

Figure 5 | SECM - Advanced Electrochemistry





Summary 1. The sulfur (S)-vacancies created on the basal plane of 2H-molybdenum disulfide (MoS_2) via electrochemistry exhibited higher intrinsic activity for the electrochemical hydrogen evolution reaction in metallic 1T-phase of MoS_2 catalysts. Even though sulfur atoms on the basal plane stable and inert, they are electrochemically reduced under accessible applied potentials. By changing the applied desulfurization potential, the extent of desulfurization and the resulting activity can be varied. 2. The resulting active sites are stable under extended desulfurization durations and show consistent HER activity measured using LSV and SECM. They are compared with pristine aerogel samples and multilayered MoS_2 signifying the role of protruded nanowalls as effective surface and edge plane sites. 3. The interplay of heterogeneous basal and edge plane sites of reduced graphene oxide and MoS_2, effective coupling of electrode/redox probe wave function and reinforce density of states in the vicinity of Fermi level facilitate efficient interfacial electron transfer. Moreover, the multiplexed three-dimensional and highly conductive pathways provided by graphene scaffold architectures also ensure rapid charge transfer. 4. Electrochemical properties elucidated efficient electron and ion transport due to larger specific surface area and charge storage capacity of rGO/MoS_2 aerogels.