Hydrogen Evolution Reaction Activity of Graphene–MoS$_2$ van der Waals Heterostructures

Ravi K. Biroju,†,∥ Deya Das,†,∥ Rahul Sharma,†,∥ Shubhadeep Pal,†,∥ Larionette P. L. Mawlong,§ Kapil Bhorkar,† P. K. Giri,§ Abhishek K. Singh,*‡ and Tharangattu N. Narayanan*,†

†TIFR-Center for Interdisciplinary Sciences (TCIS), Tata Institute of Fundamental Research, 21 Brundavan Colony, Narsingi, Hyderabad 500075, India
‡Materials Research Centre, Indian Institute of Science, Bangalore 560012, India
§Center for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati 781039, India

Supporting Information

**ABSTRACT:** Determining a suitable noble-metal-free catalyst for hydrogen evolution reaction (HER) by photoelectrocatalytic (PEC) water splitting is an enduring challenge. Here, the molecular origin of number of layers and stacking sequence-dependent PEC HER performance of MoS$_2$/graphene (MoS$_2$/GR) van der Waals (vdW) vertical heterostructures is studied. Density functional theory (DFT) based calculations show that the presence of MoS$_2$ induces p-type doping in GR, which facilitates hydrogen adsorption in the GR side compared to the MoS$_2$ side with $\Delta G_H$ closer to 0 eV in the MoS$_2$/GR bilayer vertical stacks. The activity maximizes in graphene with monolayer MoS$_2$ and reduces further for bilayer and multilayers of MoS$_2$. The PEC HER performance is studied in various electrodes, namely, single-layer graphene, single- and few-layered MoS$_2$, and their different types of vertical heterojunctions having different stacking sequences. The graphene on top of MoS$_2$ sequence showed the highest photoresponse with large reaction current density and lowest charge-transfer resistance toward HER, in agreement with the DFT calculations. These findings establish the role of stacking sequence in the electrochemistry of atomic layers, leading to the design of new electrocatalysts by combinatorial stacking of a minimal number of layers.

Recent advances in van der Waals (vdW) solids of atomic layers invoke the possibility of new types of vertical quantum heterojunctions having atomically sharp interfaces between dissimilar materials.¹ Strong covalent bonds provide sufficient in-plane stability to two-dimensional (2D) crystals, whereas relatively weak vdW interactions are sufficient to keep the stack together.¹ These vertical structures are found to have novel interface-induced physical and chemical properties.²,³ Recently, these heterostructures have also been studied for their efficacy toward electrocatalytic activities.⁴ It is established that in most of the 2D layers, basal planes (defect-free) are inactive toward any catalytic reactions.⁴ However, it is found that formation of heterostructures, where the atomic layers are placed one over the other with dissimilar atomic layers, can drastically change the inherent electrocatalytic activities of individual layers toward certain reactions, even leading to the activity of a basal plane that otherwise is inactive. It has been reported that this is due to the effect of a built-in electric field formed among the dissimilar layers or their metallic substrates.⁵−⁷ The authors have recently reported that in vdW solids-based photoelectrochemistry not only the selection of layers but also their stacking order (layer sequencing or which layer is exposed to the electrolyte or analyte) also matters in deciding the net catalytic performance.⁷ The photoelectrocatalytic (PEC) response of a few-layered MoS$_2$ and single-layer graphene was studied, and it is found that the graphene on top of MoS$_2$ (MSGR) has a PEC efficacy toward hydrogen evolution reaction (HER), $4e^- + 4H^+ \rightarrow 2H_2$, in acidic medium that is higher than that of MoS$_2$ on top of graphene (GRMS), though MoS$_2$ is the photoactive material and visible light has little effect on the PEC performance of graphene.⁷ Similar stacking sequence effect has been observed in WS$_2$/MoS$_2$ vdW vertical stacks by another research group.⁷ The mechanism leading to this new parameter called “stacking sequence” is not completely understood yet, and here a molecular mechanism for these observed effects is proposed based on density functional theory (DFT) calculations and subsequent layer-dependent HER studies.

Received: April 26, 2017
Accepted: May 9, 2017

DOI: 10.1021/acsenergylett.7b00349
ACS Energy Lett. 2017, 2, 1355−1361
Graphene–MoS$_2$ hybrids were identified as potential candidates in electrocatalysis. For example, a recent DFT study showed that the existence of a graphene layer below the MoS$_2$ has a noticeable influence on the charge density distribution of MoS$_2$. The built-in electric field in MoS$_2$–graphene hybrid forms an excessive negative charge density in the structure, which eventually enhances the HER process. Moreover, this sandwich structure can also make the basal plane of MoS$_2$ close to the thermo-neutral ($\Delta G_{\text{H}} \sim 0$), enabling the basal plane of MoS$_2$ to be active toward the HER process. Furthermore, the high optical transparency (in the visible region) and high electronic conductivity of graphene can provide efficient current injection into the MoS$_2$ layers, augmenting the PEC process. However, the observed stacking sequence-dependent PEC performance of MoS$_2$/graphene hybrids indicates that other than the interface-induced potential modification at the heterojunction resulting in an enhanced HER process, proton adsorption–desorption kinetics itself can be modified or tuned with the layer sequencing.

It has been found from the recent studies that the interface-induced effects of layer stacking are limited only to the adjacent layers; hence, stacked solids of many layers may not result in the promising effects observed in single-layered stacks. Furthermore, high-quality crystals are important to see these effects and to avoid the effects related to recombination of photocarriers. Hence, in this study, the white light PEC performances of single-layer graphene (GR), MoS$_2$ (MoS$_2$ monolayer, MSM), a few-layered (3–4 layers) MoS$_2$ (MS), and their various stacking sequences [MSGR (graphene on top of MS), GRMS (MS on top of GR), MSMGR (graphene on top of MSM), and GRMSM (MSM on top of GR)] are studied. Detailed structural and morphological characterization using field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high-resolution (HR) TEM, and atomic force

Figure 1. Structural characterization of MoS$_2$ and graphene van der Waals heterostructures. (a) FESEM images of a few-layered (MS) and single-layer MoS$_2$ (MSM) flakes. TEM image of a few-layered flake and corresponding HRTEM image and SAED pattern are shown for the MS sample. (b) Hexagonal crystalline lattice of single-layer large-area graphene (GR) and inset showing the IFFT and FFT pattern of SLG. (c, d) HRTEM images of MSGR from the same place with different focusing (top layer and bottom layer separately). Evidence for the defect-free graphene and MoS$_2$ heterostructure is revealed from the HRTEM image, and corresponding IFFT and FFT indicate the diffraction pattern of graphene and MoS$_2$, respectively. (e) Raman signatures of pristine MoS$_2$ and MoS$_2$–graphene heterostructures. (f) PL spectra of various samples. Note that the Raman and PL measurements were performed inside the Lincom cell and that the symbol '*' corresponds to the fluorescence background coming from the transparent glass of the cell.
microscopy (AFM) along with spectroscopic techniques such as photoluminescence (PL) and micro-Raman analysis are conducted to establish the stacking of layers and influence of sequencing in the photophysical phenomena.

The growth and transfer of large-area single-layer graphene to a graphite patterned polydimethylsiloxane (PDMS) substrate have been established in our previous report. The same method has been utilized in this work to obtain graphene transferred electrodes (detailed synthesis protocol is given in Methods in the Supporting Information). MoS$_2$ transferred electrodes are also developed using the same technique (polymer-assisted transfer) reported in ref7, but here care has been taken to achieve the selective transfer of single- and a few-layered MoS$_2$ samples separately. The structure of MoS$_2$ and the number of layers of MoS$_2$ on Si/SiO$_2$ are assessed from the FESEM and micro-Raman analyses, respectively. Figure 1a shows the FESEM images of a few-layered (MS) and monolayer MoS$_2$ (MSM). Most of the few-layered MoS$_2$ have polygon morphology, while in the case of the single-layer MoS$_2$, perfect triangular shape is observed, which is significant for the trigonal prismatic structure (2H phase), and usually it forms in the case of chemical vapor deposition (CVD) growth.9,10 Figure 1a (top right inset) shows the TEM image of a few-layered MoS$_2$ (MS) flake, and the bottom right inset is a high-resolution TEM (HRTEM) image of the MS. The thickness of the MS (inferred from the HRTEM image) is found to be $\sim$2−2.5 nm, indicating the presence of 3−
4 layers of MoS2, which later was confirmed by Raman and AFM analyses. The corresponding selective area electron diffraction (SAED) pattern shows the presence of hexagonal lattice diffraction spots. Before the MoS2–graphene vdW stacks were fabricated, the crystalline quality of the as-transfered CVD graphene layer was estimated from HRTEM as shown in the Figure 1b, which shows the lattice image of defect-free GR. The corresponding inverse fast Fourier transform (IFFT) (left inset) and fast Fourier transform (FFT) (right inset) are shown in the figure. Figure 1c,d shows the HRTEM image of the MSGR sample. Both the images are taken at the same location on the MSGR with different focusing and defocusing to get the top (graphene) and bottom (MS) layers individually. Note that the top and bottom insets correspond to IFFT and FFT images of graphene and MoS2, respectively. Blue and red lines in the SAED pattern denote the diffraction patterns of graphene and MoS2, respectively. Additional FESEM images of MoS2 and graphene vdW heterostructures having different stacking sequences with a few-layer and monolayer MoS2 are shown in the Supporting Information (see Figure S1). In addition, AFM topographical features of a few-layer MoS2 (MS) and MSGR are shown in Figure S2. MS has an average thickness of ~2 nm, indicating the presence of 3–4 layers, as inferred from the Raman analysis and discussed in a later paragraph. The MSGR has found to be unwashed polymer residues, which developed during wet transfer of graphene.

Figure 1e represents the Raman fingerprints of MoS2 and graphene, and the corresponding Raman spectral line shape analysis is given in Table T1. The Raman spectra of pristine layers and MSGR hybrids with monolayer and few-layered MoS2 are taken on Si/SiO2 substrates. Typical Raman signatures of GR, such as D, G, and 2D bands, are found in both samples. In the case of MoS2, E2g and A1g peak positions reveal the nature of a trigonal prismatic structure (2H-phase) of MoS2 crystals, and their peak separations (Δk) show that the number of atomic layers in the case of a few-layered MoS2 is ~3–4 layers (see Table T1).11 The average grain sizes of mono- and a few-layered MoS2 are similar, but the microstructure changes from triangular (monolayer) to a polygon shape (a few layers). This is confirmed via optical and FESEM images of MSGR and MSMGR samples taken at the same magnification, and these are shown in Figure S3. Further confirmation of the structural and excitation energy differences in the MS and MSM samples are clear from the areal Raman mappings of E2g and A1g, as shown in Figure S4. The PL spectra of pristine MSM and MS and their heterostructures with top graphene configuration are shown in Figure 1f. All the spectra are recorded with 532 nm laser excitation where the samples are kept on Si/SiO2 substrates at room temperature. Figure 1f shows the strong PL bands at around 622 and 669 nm (peak position varies depending on the number of layers),11,12 those are ascribed to “B” exciton and “A” exciton, respectively. The A exciton peak is derived from the direct band gap of MoS2, and the B exciton peak arises from the direct gap transition between the minima of the conduction band and the lower-level valence band maxima, where it is created by strong valence band spin–orbit splitting at the K point.3,13,14 It is evident from Figure 1f that the PL intensities (622 and 669 nm) of single-layer MoS2 (MSM) are enormously strong in comparison to a few-layer system in both pristine and vdW heterostructures. A detailed description of the stacking sequence-dependent PL evolution of MoS2–graphene vdW structures was reported elsewhere. Gaussian line shape analysis of PL bands A and B reveals the information about the interlayer interactions and spin–orbit coupling when they form heterostructures,15 as shown in the Table T2. The integrated intensity ratio of A and B PL peaks (I_A/I_B) in MSMGR is ~5 times higher than that of all the samples including MSGR, indicating formation of a significant amount of photoexcitons in MSMGR. Hence, Raman and PL analyses show that photophysical phenomena of MoS2 can be varied with respect to the number of layers and their stacking with other layers such as graphene.

The HER performance of various working electrodes (graphite patterned PDMS substrates; schematic of the working electrodes is given in the inset, Figure 2) modified with atomic layers (MS, MSM, and GR) and their hybrids (GRMS, MSGR, and MSMGR) are studied using three-electrode linear sweep voltammetry (LSV, details are given in Methods in the Supporting Information). All the LSV measurements both in dark and light conditions (white light, wavelength range from 370–730 nm) are carried out in 0.5 M H2SO4 solution at a scan rate of 10 mV s⁻¹. Figure 2a shows the LSVs of PEC HER reaction using MSGR and GRMS and comparison of their photocurrent enhancement with respect to dark. The HER Tafel slopes with different electrodes are plotted in Figures S5, and they show variation with respect to different electrodes as well as light and dark conditions. However, it has been shown (in our earlier report and other recent reports)7 that Tafel slopes cannot give a proper measure of kinetics in the case of an evolution reaction. Here the current densities are calculated using the geometrical area of the working electrode containing the transferred 2D layers. The charge-transfer kinetics of the inner redox probe [Fe(CN)6]⁴⁻/³⁻ on various working electrodes are calculated (Figure S6) and the electrochemical area of the electrodes are calculated using the Randles–Sevcik equation (details in the Supporting Information). The LSVs, where the current densities are calculated using electrochemical surface area (instead of geometrical area), are given in Figure S7. These indicate that the drastic enhancement in the reaction current densities are not from the differences in the geometrical area of the electrodes. As observed before,7 MSGR provides the best PEC performance compared to other geometries. Due to the high surface area of MSGR, a high Faradaic contribution is seen while considering the geometrical area for current density calculations (Figure 1a), but it is not there while taking electrochemical surface area (Figure S7). The HER LSV experiments are extended to MSM, MSMGR, and GRMSM, where single-layer MoS2 (MSM) is used. The results are shown in Figure 2b. The LSV of the benchmarked HER catalyst, Pt/C, is compared in both cases.

As it has been reported, in the case of MS, the HER reaction starts at an onset potential of ~−0.45 V (RHE).7 In the presence of light (LSV in light is taken after 45 min of light exposure in all cases), the onset potential shifts to a lower potential (~−50 mV change) along with a drastic enhancement in the current density, indicating the generation of photocarriers in MS after the exposure of light and the augmented reduction process of adsorbed proton. The GR electrode has only a nominal HER response, having an onset potential of ~−0.55 mV with very low current density, and has no light-induced carrier generation. The GRMS electrode shows an onset potential (with a little drop in the current density) similar to that of MS while in MSGR, the current density is drastically enhanced upon illumination of white light. In the cases of MSM samples, the same trend is observed with a little decrease in the current density (calculated using geometrical area). The decrease in the current density is due to the smaller amount of MoS2 in MSM in a given electrode.
area, as is shown in Figures 1a and S1 (areal density of layers is less, as inferred from FESEM data).

The light response of individual structures is further distinguished by calculating the ratio of current densities ($J_{\text{light}}/J_{\text{dark}}$) at −0.6 V (RHE) of each geometry (the values are given in Table T2), and the corresponding values are given in the bar diagram (Figure 2c). It can be seen from the Figure 2c that the light response is highest for MSMGR, and this is much higher than that of MSGR. This indicates that the light-induced activities are much higher in heterojunctions having fewer layers (here bilayer), which is further established in the DFT analysis.

To probe further into the HER performance of various samples, electrochemical impedance spectroscopy (EIS) measurements are performed on each sample in dark and light conditions at −0.4 V (vs RHE, with an input sine wave having 10 mV amplitude) where the HER is supposed to be just initiated (onset potential). EIS is identified as a powerful technique to probe the heterogeneous electron-transfer rate both in light and dark HER conditions.7 Figure 2d shows the Nyquist plots of GRMS and MSGR in dark and light conditions. The inset shows the magnified view of the MSGR in light exposure, showing the charge-transfer resistance ($R_{ct}$). This impedance plot is fitted with a Randles circuit (the dotted lines correspond to experimental values, and the solid line corresponds to the fitting). The Randles circuit consists of solution resistance ($R_1$), charge-transfer resistance ($R_2$ or $R_{ct}$), constant phase element ($Q_2$), and diffusion of ions in electrolyte solution represented by Warburg region ($W_2$). After fitting with the above circuit, $R_{ct}$ has been estimated. Among all the samples (MSGR and GRMS), MSGR showed the lower $R_{ct}$ value in dark conditions. Upon illumination, the $R_{ct}$ value of MSGR is further reduced to 0.08 kΩ (80 Ω), indicating the augmented charge-transfer process in the presence of light. The $R_{ct}$ values of GRMS were also decreased upon illumination, indicating the presence of light-generated carriers in these electrodes, but charge-transfer resistance is quite high compared to that of MSGR.

The EIS studies of single-layer MoS$_2$-based samples are shown in Figure 1e, and all the measurements are carried out at −0.4 V (vs RHE). The corresponding Randles circuit fitting is also shown in each curve. It is observed that $R_{ct}$ values of MSMGR and GRMSM (both in light and dark conditions) are much lower than those of the corresponding MSGR and GRMS samples. MSMGR has the lowest $R_{ct}$ (30 Ω). For further comparison, $R_{ct}$ values of various electrodes under light exposure are shown in Figure 1e. It can be seen from Figure 1e that MSMGR (MSGR is next highest) has the lowest $R_{ct}$ among various geometries. This indicates that both the number of layers and their stacking sequence affect the efficacy of the HER process.

To understand the mechanism behind the enhanced catalytic activity in graphene/MoS$_2$ heterostructures, theoretical hydrogen adsorption has been studied using first principles-based DFT calculations. The heterostructure having one layer of MoS$_2$ and graphene (bilayer system) is shown in Figure 3a, and the band structure of this system along with density of states (DOS) is plotted in Figure 3b. When graphene forms vertical heterostructure with MoS$_2$, the Dirac cone at K point remains

---

Figure 3. (a) Bilayer heterostructure of graphene and MoS$_2$, where cyan, yellow, and black denote Mo, S, and C atoms, respectively. (b) Corresponding band structure and density of states. Side and top view of hydrogen adsorption (c) on graphene side and (d) MoS$_2$ side, where hydrogen is denoted by a red sphere. (e) Plot of $\Delta G_H$ for hydrogen adsorption in both of these cases.
unaltered, making the system metallic. However, the Fermi level shifts lower, leading to p-type doping in graphene. The conduction band at the $\Gamma$ point comes from the MoS$_2$ layer, and it touches the Fermi level, indicating that charge transfer happens from graphene to MoS$_2$.

Hydrogen adsorption has been studied in the bilayer heterostructure both in the graphene side and in the MoS$_2$ side, as shown in Figure 3c,d. Gibbs free energy ($\Delta G_{\text{H}}$) for hydrogen adsorption on a catalyst should be closer to zero to ensure the best electrocatalytic activity. In the graphene side, hydrogen adsorbs on the top of a carbon atom having a bond length of 1.12 Å, and as a result, the corresponding carbon atom protrudes out of the graphene plane. On the other hand, in the case of the MoS$_2$ side, hydrogen prefers to adsorb almost at the center of the MoS$_2$ hexagon. The values of $\Delta G_{\text{H}}$ are plotted in Figure 3e for both the cases, and it is found that hydrogen adsorption is preferable on the graphene side ($\Delta G_{\text{H}}$ of 1.45 eV) compared to on the MoS$_2$ side (2.01 eV).

In order to determine the reason behind the preference of hydrogen adsorption on the graphene side, the band structures and DOS for both the cases have been calculated, as plotted in Figure 4a,b. When hydrogen is adsorbed in the graphene side, the sp$^2$ bonded carbon becomes sp$^3$ hybridized, which destroys the linear band dispersion of pristine graphene (see Figure 3a). The conduction band of pristine graphene, lying at the Fermi level, almost becomes dispersionless. Similarly, in the case of hydrogen adsorption on the MoS$_2$ side, the conduction band coming from MoS$_2$ in the heterostructure shifts lower toward the Fermi level and becomes almost dispersionless (Figure 3b). The linear dispersion of graphene at the K point remains unchanged. From the DOS studies, H 1s states are found at the Fermi level, similar to the previous case. Graphene being p-type doped takes an electron from atomic hydrogen, thereby showing stronger adsorption energy than the adsorption on MoS$_2$ side. It has been further confirmed by calculating charge accumulation and depletion, as shown in Figure S8. Being a vdW heterostructure, there is no charge transfer between the layers, as expected. When hydrogen is adsorbed on the graphene side, hydrogen depletes more compared to the case of hydrogen adsorption on the MoS$_2$ side. Moreover, in the case of hydrogen adsorption on the MoS$_2$ side, Mo atoms accumulate only the charge from hydrogen. Therefore, hydrogen adsorbs strongly on the graphene side because of more charge transfer compared to the other case.

The effect of the number of MoS$_2$ layers in the hydrogen adsorption is further investigated by increasing the number of MoS$_2$ layers. In the presence of more MoS$_2$ layers, the Dirac cone of graphene splits (shown in Figure 4c for two layers of MoS$_2$) as the sublattice symmetry of graphene breaks because of the interaction with MoS$_2$ layers. However, the graphene remains p-type doped, and because of the change in symmetry, the Brillouin zone changes, leading to changes in high-symmetry points. In graphene with two layers of MoS$_2$, the direct band gap of MoS$_2$ at the $\Gamma$ point reduces to 1.12 eV from 1.59 eV for graphene with monolayer MoS$_2$. The reduction in band gap with increasing number of MoS$_2$ layers is in good agreement with PL measurements, where the A peak has been found to be shifted toward the higher wavelength region (Figure 2f). The values of $\Delta G_{\text{H}}$ have been plotted as a function of the number of layers, as
shown in Figure 4d. For hydrogen adsorption on the graphene side, the values of $\Delta G_H$ decrease with increasing number of MoS$_2$ layers. On the other hand, it increases for the adsorption on the MoS$_2$ side. However, the values of $\Delta G_H$ remain almost same for two and three layers of MoS$_2$, denoting the bulk limit. Hence, hydrogen adsorption becomes most preferable on the graphene side for the bilayer graphene/MoS$_2$ heterostructure.

In conclusion, the HER process in an acidic medium is studied with atomic layers of graphene (single layer) and MoS$_2$ (single-layered and a few layers) and their van der Waals vertical heterostructures of different stacking sequences (MSGR, GRMS, MSMGR, and GRMSMS), and these geometries are characterized using electron microscopy. All the electrochemical measurements are carried out in a graphite patterned PDMS substrate to avoid interference from the substrate. In both the single- and multilayered MoS$_2$ samples, graphene on top of MoS$_2$ (i.e., MSMGR and MSGR) showed the highest photoresponse and HER activity, indicating the role of stacking sequence in HER performance of MoS$_2$/graphene heterostructures. MSMGR showed a photoresponse higher than that of MSGR, with the highest $I_{light}/I_{dark}$ (at $-0.6$ V) and lowest R$_C$ value (30 $\Omega$ for MSMGR and 80 $\Omega$ for MSGR) in EIS measurements. DFT calculations explained the underlying mechanism of this enhancement in catalytic activity in MSMGR as the charge transfer from graphene to MoS$_2$ results in p-type doping in graphene, leading to $\Delta G_H$ for hydrogen adsorption on the graphene side being closer to zero. This study shows that the band engineering and tuning of the HER kinetics of layered structures can be obtained via noncovalent interactions, unlike the case of other structures, such as carbon nanotubes, where covalent functionalization is found to be changing the HER kinetics and dispersion at the Fermi level, aiding an augmented HER process.\textsuperscript{17}

**REFERENCES**