Van der Waals hetero-structures of 1H-MoS2 and N-substituted graphene for catalysis of hydrogen evolution reaction

Lakshay Dheer1,2, Satadeep Bhattacharjee1, Seung Cheol Lee3 and Umesh V Waghmare4,5

1 Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India
2 Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India
3 School of Advanced Materials, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India
4 Indo Korea Science and Technology Center, Korea Institute of Science and Technology, Bangalore 560065, India
5 Sheik Saar Laboratory, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India

E-mail: waghmare@jncasr.ac.in

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Abstract

First-principles theoretical analysis of the catalytic activity of van der Waals hetero-structures of 1H-MoS2 and graphene substituted with three chemical types of nitrogen species (i) Graphitic (G), (ii) Pyridinic (Pn) and (iii) Pyrrolic (Pr), for application in catalysis of hydrogen evolution reaction (HER) has been presented. Graphitic and pyrrolic N substituents result in n-type electronic structure, whereas substitution of pyridinic N imparts p-type electronic character to the hetero-structure. Work functions (ϕ) of the hetero-structures suggest that graphitic N-graphene:MoS2 hetero-structure (ϕ = 3.8 eV) is expected to be effective in catalysing the reduction of H+ to evolve H2. 1H-MoS2 monolayer in the hetero-structure contributes by enabling increased H2O adsorption and offsetting the band edge energies optimal for the catalytic activity. Near optimum Gibbs free energy of H-adsorption (∆GH) were obtained for graphitic (∆GH ≈ 0.29 eV) and pyrrolic (∆GH ≈ −0.2 eV) N-graphene:MoS2 hetero-structures. Our work showcases how catalytic and electronic properties of the N-doped graphene:MoS2 hetero-structure depends on the chemical identity of N-sites and uncovers a route to 2D hetero-structures with high catalytic activity.

1. Introduction

Graphene [1], a 2-dimensional sheet of sp2 hybridized carbon atoms, initiated intense research activity in the field of 2D materials. In addition to exhibiting exceptional in-plane tensile strength [2] and a large specific surface area [3], graphene also exhibits properties such as high electrical and thermal conductivities [4, 5], good transparency [6], due to its unique electronic structure and high in-plane elastic stiffness. Being atomically thick, graphene serves as a perfect candidate to form hetero-structure with other 2D materials. Another well studied 2D-material is molybdenum disulfide (MoS2) [7], a member of the family of Transition Metal Dichalcogenides (TMDCs). MoS2 is widely used in solid-state lubrication, photovoltaic devices, and rechargeable batteries [8]. Bulk 2H-MoS2 comprises of S-Mo-S monolayers which are held together by van der Waals interactions [9].

Recently, exciting research has emerged in exploration of hetero-structures formed by stacking or adjoining different 2D materials together [10]. These 2D crystals can be coupled in a horizontal fashion creating an in-plane interface or by stacking them on top of one another forming a vertical hetero-structure. An attractive feature of these hetero-structures is that each layer acts as a bulk 2D material and an interface simultaneously [11]. These vertical hetero-structures are held together by van der Waals interactions and are known to showcase novel interface-induced physical and chemical properties [12]. A particularly well-studied hetero-structure is graphene:MoS2 hetero-structure [12–15] which was first fabricated by Chang et al [16]. This stacked graphene:MoS2 hetero-structure has recently been exploited for its catalytic activity towards the HER. Hydrogen evolution reaction (HER) is the reduction involved in the water splitting reaction and gives hydrogen (H2) as the...
product. H₂ is an attractive fuel for storage of energy in the form of chemical energy. One of the challenges in use
of hydrogen is the scarcity of earth abundant materials to catalyse the conversion of protons (H⁺) to H₂.

Li et al showed that graphene layer as a support couples electrically with MoS₂ hence affecting the charge
density distribution in MoS₂ [17]. The stacking leads to an in-built electric field in the hetero-structure resulting
in excess negative charge on MoS₂ monolayer which improves its electrocatalytic activity towards HER.
Similarly, a significant increase in the activity of inert MoS₂ surface was reported when graphene oxide (GO) was
used as a support [18]. The catalytic activity of MoS₂ basal plane was influenced by the oxygen concentration in the
GO. N-doping in the GO substrates further enhanced the catalytic activity giving a ΔG_{II} ∼ −0.014 eV [18]. A recent report by Biroju et al [12] discussed the p-type doping effect of MoS₂, which promotes the
hydrogen adsorption on the graphene side of the graphene:MoS₂ hetero-structures.

Substitutional N-doping in graphene [19] is known to tune the electronic spectrum and enhancing its
properties for various applications [20]. While there have been many theoretical [12, 21, 22] and experimental
[12, 23] works on graphene:MoS₂ hetero-structures, effects of N substitution in graphene on the catalytic and
electronic properties of the hetero-structure have not been investigated yet.

Here, a detailed theoretical analysis of nitrogen (N)-doped graphene:MoS₂ bilayered hetero-structures,
considering three different chemical types of N substituent: (i) Graphitic (G), (ii) Pyridinic (Pn), and (iii) Pyrrolic
(Pr) is presented. Our focus is on the effects of chemical nature of N on the catalytic activity of graphene:MoS₂
hetero-structure. It is observed that the chemical type of substitutional N greatly influences the frontier
electronic states of a hetero-structure whereas the interlayer binding and distance are about the same. Work
function (Φ) of such a hetero-structure is thus dependent on the chemical type of N substituent; G N-atoms lower the Φ (n-type doping) while Pn N-atoms as well as Pr N-atoms increase the Φ (p-type doping) of the
hetero-structure. Pr N-doped graphene:MoS₂ hetero-structure is a direct narrow gap semiconductor with a
band gap value (Eₐ) of ∼266 meV. Catalytic activity of graphene:MoS₂ towards HER enhances with
N-substitution as the Gibbs free energy for hydrogen adsorption reduces from ΔG_{II} ∼ 1.27 eV for pristine
hetero-structure to ΔG_{II} ∼ −0.2 eV and ΔG_{II} ∼ 0.295 eV for pyrrolic and graphitic N-doped
graphene:MoS₂ hetero-structures.

2. Results and discussion

Lattices of MoS₂ and graphene monolayers have a nontrivial size mismatch. To construct a model hetero-
structure, we place a 5x5 supercell of graphene on a 4x4 supercell of 1H-MoS₂, with a C atom of graphene placed
on top of one of the Mo atom of the MoS₂ sheet. It was previously shown that relative in-plane translation of
graphene over the MoS₂ monolayer neither affects the energetics, nor the electronic properties of the system
[21]. This is because local chemical environment of atoms averages out due to use of large supercell containing
5x5 units of graphene and 4x4 units of MoS₂. To determine the properties of N-graphene:MoS₂ hetero-structure
we considered three configurations: the 'graphitic' N corresponds to simply replacing a C atom by N atom in the
graphene layer. In G N-graphene:MoS₂ (figure 1(b)) we replace 6% C atoms of the graphene sheet with N atoms
and place them far from each other to keep the interaction between the N atoms weak. The 'pyridinic' and
'pyrrolic' N, atoms which contribute one and two electrons each respectively to the π conjugated system [24]. Pn
N-graphene:MoS₂ (figure 1(c)) comprises of three pyridine rings with 6% N-substitution and 2% vacancies in
the graphene sheet creating a pyridine-like local chemical environment for N atoms. Similarly, the Pr
N-graphene:MoS₂ (figure 1(d)) structure is obtained with two N atoms inducing pyridine rings and one N atom
forming a 5-membered pyrrole ring. A hydrogen (H) atom bonding with N atom is introduced to satisfy the
valency of pyrrolic N substituent.

2.1. Interlayer spacing

The optimum interlayer spacing between the two monolayers is obtained by minimizing binding energy (Eₘ)
between the N-doped/pristine graphene and MoS₂ monolayers:

\[ Eₘ = Eₘ – \text{Graphene/pris:MoS}₂ – (Eₘ – \text{Graphene/pris} + E_{MoS₂}) \]

where \( Eₘ – \text{Graphene/pris:MoS}₂ \), \( E_{MoS₂} \), and \( Eₘ – \text{Graphene/pris} \) are the energies of the hetero-structure, isolated 1H-MoS₂
(4 × 4), and isolated N-doped/pristine graphene monolayer (3x5), respectively (see table 1 and figure S2 is
available online at stacks.iop.org/MRX/6/124006/mmedia). It is evident that the optimum separation is about
3.4 Å which is in good agreement with earlier reports [15, 21]. The vdW forces are almost solely responsible for
the adhesion between the monolayers (table S1). Regardless of the chemical nature of substituted N, \( Eₘ \) changes
by only about ∼10% (table 1) showing that N-doping does not strongly affect the strength of adhesion of
graphene sheet on MoS₂.
2.2. Electronic properties

To understand the effect of chemical nature of N on the electronic properties of these graphene:MoS₂ heterostructures, we determine the electronic structure and projected density of states (PDOS) (see figure 2). Electronic structure of pristine graphene:MoS₂ hetero-structure is a simple superposition of electronic structures of each component (figure 2(a)). Graphene retains the linear dispersion of its bands and the Dirac point falls in the energy gap of 1H-MoS₂. Interestingly, the Dirac point of graphene shows a tiny gap (~2.8 meV), consistent with the report by Ma et al [21]. The orbitals of the C atoms of graphene contribute to states at energies between those of Mo-4d and S-3p orbitals as seen in the PDOS of the hetero-structure (figure 2(a)).

Electronic structure of the graphene:MoS₂ hetero-structure changes with the chemical nature of N-substituents remarkably. Replacing three C atoms of 5x5 supercell of graphene with N atoms (graphitic N-substitution) (figure 1(a)) results in donation of electrons causing the $E_F$ to shift up, imparting n-type character to the hetero-structure. States arising from N-substituents can be seen just above the Fermi level ($E_F$) in the PDOS (figure 2(b) inset). With a small gap (~0.1 eV) opening up at the Dirac point, dispersion of bands at the Dirac point is parabolic in nature. This is evident in all the N-doped hetero-structures studied here irrespective of the chemical identity of N-atom.

Our configuration of graphitic N-substitution differs from that with pyridinic (Pn) N in the sense that in the former, N atoms are intentionally kept away from each other so as to lessen the N-N interaction (figure 1(b)). In Pn-N substitution, three N atoms are placed in close vicinity to each other and a vacancy defect is introduced at the centre of these dopants breaking the $\pi$ conjugation and creating a pyridine ring like environment (figure 1(c)). Here, two of the five valence electrons of N participate in $\sigma$ bonding with the neighboring C atoms while one contributes to $\pi$ state within the pyridine ring. The remaining two electrons form a lone pair as the $\pi$ conjugation is absent due to the vacancy adjacent to the dopants, and this lone pair gives rise to two new bands just below the $E_F$ (see figure 2(c)). The Pn-N doping shifts the $E_F$ down relative to the Dirac point, imparting
effectively a p-type character to the hetero-structure. A gap (~0.48 eV) opens up at the Dirac point and the dispersion of resulting bands is parabolic.

Pr N-graphene:MoS$_2$ hetero-structure consists of two pyridine rings and one pyrrole ring in the supercell of graphene lattice (figure 1(d)). Pyrrolic-N atom uses three of its five valence electrons in $\sigma$ bonding, two with C atoms and one with H atom, the remaining two electrons are delocalized, imparting the pyrrole ring its aromatic nature. Therefore, the pyrrolic-N atom lends two electrons to the $\pi$ conjugated system, imparting an n-type character to the system. Whereas two Pn- N atoms present in the sheet promote p-doping with downward shift in $E_F$ as explained earlier. The opposite effects of the two types of N atoms (figure 2(d)) cancel each other out resulting in a small band gap opening at the Dirac point, and thus Pr N-graphene:MoS$_2$ hetero-structure is a direct narrow band gap semiconductor (figure 2(d)) with a band gap ($E_g$) of ~266 meV.

Further the work function ($\varphi$) which is defined as the minimum amount of energy required to remove an electron from a material to vacuum, and was recently shown to be relevant to the reactivity of a catalyst [25] is calculated. To estimate work functions of pristine graphene:MoS$_2$, graphitic N-graphene:MoS$_2$, and pyridinic N-graphene:MoS$_2$ hetero-structures the following expression is used

$$\varphi = V_{vac} - E_F,$$

and for pyrrolic N-graphene:MoS$_2$

$$\varphi = V_{vac} - E_{VBM},$$

where $E_{VBM}$ and $V_{vac}$ is the energy of valence band maximum and vacuum energy respectively. $\varphi$ is used to align the energies of band edges with respect to vacuum and hydrogen evolution potential (HER) (figure 3) to assess the suitability of these graphene:MoS$_2$ hetero-structures as catalysts for hydrogen evolution. Doping graphene with graphitic N-atoms reduces the $\varphi$ of the hetero-structure, while Pn and Pr N-substitutions increase the $\varphi$ (see table 1). The hydrogen evolution potential (HER) is just below $E_F$ (figure 3) of graphitic N-graphene:MoS$_2$, suggesting it to be a viable electrocatalyst for HER. Pristine, Pn N-substituted and Pr N-substituted graphene:MoS$_2$ hetero-structures, due to appropriate band edge energies, are predicted to be photocatalysts for HER (figure 3). To check the viability of the pristine and the N-substituted graphene:MoS$_2$ hetero-structures as photocatalysts, we obtained their optical conductivities. All the four hetero-structures show absorbance in the visible part of the spectrum, mainly blue-violet light (see figure S5), showing their suitability to use solar energy. To understand the role of MoS$_2$ in the hetero-structures, we align the projected band edge energies of pristine and N-doped graphene monolayers on the SHE potential scale (see figure 3). As is evident here, MoS$_2$ support shifts $E_F$ down and increases the work function of the pristine as well as N-substituted graphene monolayers (see table S2). To understand electronic properties at the graphene:MoS$_2$ interface of the hetero-structures, we

Figure 2. Electronic structure and projected density of states (PDOS) of a) Pristine graphene:MoS$_2$, b) graphitic N-graphene:MoS$_2$, c) pyridinic N-graphene:MoS$_2$, and d) pyrrolic N-graphene:MoS$_2$. An overlapping electronic structure of graphene and MoS$_2$ is observed (a), n-type character in graphitic N-doped graphene:MoS$_2$ (b), defect bands of N and p-type character in the valence band of graphene (c), and a gap opened up in graphene bands in (d). Doted cyan line denotes the Fermi level.
examine the planar average charge density difference. Charge transfer across the interface between two monolayers (pristine/N-graphene and 1H-MoS2) is evident as an excess negative charge accumulates on the 1H-MoS2 monolayer (figure S3). This leads to built-in electric field at the interface, consistent with the observation made by Li et al[17]. Interestingly, the trend in charge transfer characteristics correlates with the work function of four hetero-structures studied here, i.e., higher the charge accumulation on the MoS2 monolayer, lower is the work function. For graphitic N-graphene:MoS2, a relatively larger charge transfers from N-graphene to the MoS2 monolayer, reflecting in charge accumulation on the MoS2 lattice, correlating with its low work function.

2.3. Simulations of adsorption
To quantify the catalytic performance of these hetero-structures, the strength of adsorption of H-atom, H2O molecule and OH at various adsorption sites on the N:graphene side of four hetero-structures (see figure 1) is obtained. The interaction strength between the adsorbate and the surface is evaluated using:

$$\Delta E_{\text{ads}} = E_{\text{complex}} - (E_{\text{heterostructure}} + \mu_{\text{adsorbate}})$$

where $\Delta E_{\text{ads}}$ is the adsorption energy and $E_{\text{complex}}$, $E_{\text{heterostructure}}$, $\mu_{\text{adsorbate}}$ are the total energies of adsorbate-heterostructure complex, hetero-structure, and chemical potentials of isolated adsorbate (H-atom, H2O and OH), respectively. Here, $1/2\mu_H$ and $\mu_{H2O} - 1/2\mu_H$, are taken as the chemical potential of an isolated H-atom ($\mu_H$) and OH ($\mu_{OH}$), respectively. Doping graphene with N strengthens the hydrogen adsorption and the effect varies with the chemical nature of N dopant (table S3). Analysis of the projected density of states (PDOS) of H-atom adsorbed (site 1, figure 1) on pristine and N-doped graphene:MoS2 hetero-structure (figure 4) reveal the nature of interaction between the highest occupied molecular orbital (HOMO) of the adsorbate (H) with the bands of the catalyst. The HOMO peak of adsorbate on pristine graphene:MoS2 hetero-structure lies at $E_F$ (see figure 4(a)) showing its weak interaction with the C-2p orbital of the substrate. In graphitic N-graphene:MoS2, the HOMO of adsorbed H-atom is fully occupied and lies below the $E_F$ (see figure 4(b)). Also, the associated peak (HOMO) in PDOS splits and becomes broad showing its covalent interaction with the graphitic N-substituents. The HOMO peak of H-atom adsorbed on pyridinic N-graphene:MoS2 hetero-structure is sharp and lies just above $E_F$ (see figure 4(c)), resonant with the N states, resulting in weaker adsorption. Relatively high $\Delta E_{\text{ads}}$ at sites 2, 3 and 4 of pyridinic N graphene:MoS2 hetero-structure are due to the vacancy defect present in the graphene ring. H-atom adsorbs strongly at the N-atom vacancy site, and increases (in magnitude) the energy of adsorption (see figure S5). The HOMO peak of H-atom attached to the pyrrolic N (dashed dark green peak) and the HOMO of adsorbed H, both lie much deeper in energy and resonate with the pyrrolic N-atom (see figure 4(d)). The adsorbed H-atom, prefers to bind to the electron rich N site which leads to the H-atom attached to the pyrrolic N being pushed out of plane (see figure 4(d) inset). This is also shown in the iso-surfaces of wave functions where the HOMO of the adsorbed H-atom is interacting with the N-2p orbital (see figure S7) which enhances the strength of adsorption (see figure S4). The binding of H2O to the graphene:MoS2 hetero-structures remains relatively unaltered on introduction of N-substituents. Poisoning of the catalytically active sites by OH (in alkaline media) is unlikely for both pristine and N-substituted hetero-structures since $\Delta E_{\text{ads}}$ is positive for all cases considered here.

Figure 3. Energies of electronic band edges of N-substituted graphene monolayers (green) and of hetero-structures projected on to graphene (red) and MoS2 (blue) aligned to vacuum and hydrogen evolution potential (HER) and oxygen reduction potential (OER). Black circles denote the Fermi energy. Yellow and cyan panels represent the band gaps at the K and Gamma points. Vacuum potential is set to 0 eV.
Adsorption of H$_2$O molecule on N-graphene monolayer was also simulated to get deeper understanding of role of MoS$_2$ on catalytic nature of the hetero-structure. The adsorption of H$_2$O molecule at the considered adsorption sites 1, 2 and 3 (see figure 1(c)) of Pn N-graphene was simulated. The interaction between the adsorbate and monolayer is weaker in magnitude as compared to hetero-structure (table S4).

Gibbs free energy of H adsorption ($D^G_H$) has been widely used as a descriptor of catalytic activity towards HER, and its value close to zero is optimal [26]. To calculate $D^G_H$, we use:

$$D^G_H = \Delta E_{\text{ads}}^H - T \Delta S_H + E_{ZPE}^H$$

where, $\Delta E_{\text{ads}}^H$ is the H-adsorption energy, $\Delta S_H = 1/2S_H^0 - S_H$ being the entropy of H$_2$ molecule [27] and $E_{ZPE}^H = 1/2E_{2\text{H}_2}^H - E_{ZPE}^{2\text{H}_2}$ being the zero-point energy of an isolated H$_2$ molecule [27]. At T = 298 K, $\Delta G_H$ of H at site 1 of graphitic N-graphene:MoS$_2$ hetero-structure is $\sim$ 0.295 eV, while that at sites site 2 and 3 of pyrrolic N-graphene:MoS$_2$ hetero-structure is $\sim$ $-$ 0.2 eV (see figure 5 and S8). For H-adsorption on pristine graphene:MoS$_2$ hetero-structure, $\Delta G_H$ $\sim$ 1.27 eV, which is comparable to the estimate reported recently by Biroju et al ($\Delta G_H = 1.45$ eV) [12].

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**Figure 4.** Projected density of states (PDOS) of H-atom adsorbed on a) Pristine graphene:MoS$_2$, b) graphitic N-graphene:MoS$_2$, c) pyridinic N-graphene:MoS$_2$, and d) pyrrolic N-graphene:MoS$_2$, at adsorption site 1. Inset shows optimized structures of H-adsorbed on respective hetero-structures (see figure S4 for complete structures). Dotted black line denotes the Fermi level. Cyan boxes show the HOMO of adsorbed H-atom. Carbon, nitrogen and hydrogen atoms are represented by grey, blue and green spheres respectively.

**Figure 5.** Volcano plot of DFT-calculated Gibbs free energies of H adsorption and experimentally measured exchange current, Log $i_0$. Plot recreated using data from [28]. The blue circle and red square/green diamond correspond to $\Delta G_H$ for graphitic and pyrrolic N-graphene:MoS$_2$ respectively.
3. Conclusions

It is concluded that the electronic properties of graphene:MoS$_2$ hetero-structures can be tuned with different chemical types of N-doping. The graphitic N-doped hetero-structure exhibits optimal band edge positions for reduction of H$^+$ to evolve H$_2$. Calculated Gibbs free energies of H adsorption ($\Delta G_{HI}$) show that N dopants strengthen the adsorption of H-atom on the hetero-structure, and nearly optimum interaction energies are obtained for graphitic and pyrolic N-graphene:MoS$_2$ hetero-structures, $\Delta G_{HI} \sim 0.295$ eV and $\Delta G_{HI} \sim 0.2$ eV, respectively. It is also shown that using 1H-MoS$_2$ as a support strengthens the adhesion between the adsorbate (H$_2$O) and hetero-structure, and also imparts a p-type character to the hetero-structure. The graphene:MoS$_2$ hetero-structures are shown to be photocatalysts for HER due to suitable band edge energies and absorbance in the visible part of solar spectrum. Another subtle result is that a tiny gap ($\sim 2.8$ meV) opens up at the Dirac point of pristine graphene over 1H-MoS$_2$, consistent with the reported value [21]. These results offer useful insights into deciphering and enhancing catalytic activity of vdW hetero-structures by substitutional doping.

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ORCID iDs

Lakshay Dheer \(\text{https://orcid.org/0000-0002-2196-2589}\)
Satadeep Bhattacharjee \(\text{https://orcid.org/0000-0002-6717-2881}\)

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