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We discovered the in situ generation of S-doped carbon sandwiched between the MoS$_2$ nano-sheets during pyrolysis of Mo(VI)-polydopamine (PDA) in presence of elemental sulfur. This causes enrichment of MoS$_2$ with more edge planes (2H $\rightarrow$ 1T), also resulting in enhanced charge density and electronic conductivity. The phase transformed MoS$_2$[@S$_x$-PDA] exhibits enhanced HER activity with $\eta$ = 160 mV at a current density of 10 mA cm$^{-2}$.

Hydrogen represents one of the most promising clean energy sources. For its efficient production through electrochemical hydrogen evolution reaction (HER), metal alloys, enzymes, metal dichalcogenides, metal oxides and a few molecular electrocatalysts have been reported. Molybdenum disulfide (MoS$_2$) promises an earth-abundant, low-cost alternative to the precious metals. Considerable effort has been invested to investigate and optimize the catalytic activity of various MoS$_2$ materials in the form of nanoparticles, mesoporous forms, amorphous and doped MoS$_2$, thin solid films, graphene-supported MoS$_2$ heterostructures, and chemically exfoliated layers. HER on bulk MoS$_2$ requires high overpotentials due to its poor intrinsic electronic conductivity and low crystallinity. It was later found that edge planes in MoS$_2$ have more unsaturated sulfur than the basal planes which are responsible for the increased activity towards hydrogen evolution reaction. It was suggested that the edge site and metallic 1T polymorph of MoS$_2$ materials are catalytically active. It has been recently shown that conversion of semiconducting 2H MoS$_2$ (trigonal prismatic) to metallic 1T (octahedral) phase improves the HER catalytic performance, but the mechanism responsible for the enhancement is present not fully elucidated. Example, it is unclear if the enhancement in the catalyst properties is related to increased conductivity of the nano-sheets that can facilitate charge transfer kinetics or if the metastable metallic 1T phase of MoS$_2$ is intrinsically more active. Motivated by these findings, we reasoned that simultaneous increase in electrical conductivity and transformation of MoS$_2$ to its 1T phase will lead to an electrocatalyst with exceptional properties suitable for HER. In recent years, mussel-inspired adhesive surface coatings based on catecholamines such as dopamine, 3,4-dihydroxyphenylalanine (mimic of mytilusedulis foot protein Mefb-5) are attractive due to their adhesion to diverse substrates, biocompatibility etc. These catecholamine based monomers undergo self-polymerization under mild alkaline conditions or chemical oxidation. The available knowledge suggests that the polymer is made up of polyindole units. Polydopamines are used for simultaneous reduction and functionalization of carbon substrates such as graphene oxide, carbon nanotubes (CNT) and used in energy storage/conversion device fabrication. In addition to all these excellent physicochemical properties, PDA yields sp$^2$-rich graphite like carbon upon carbonization under inert atmosphere at elevated temperatures.

In this work, we report the discovery of the 1T phase-enrichment and its stabilization within the MoS$_2$ nano-sheets, taking advantage of incorporation of in situ generated S-doped carbon. In this approach, the PDA-bound molybdate was pyrolyzed in presence of elemental sulfur. The obtained MoS$_2$[@S$_x$-PDA] exhibits excellent electrical conductivity, high crystallinity and more importantly, the formation of 1T phase with more edge planes. The MoS$_2$[@S$_x$-PDA] exhibited high electrocatalytic activity towards HER at low overpotential. Mo(VI) on polydopamine [Mo(VI)@PDA] was synthesized by mixing ammonium molybdate and dopamine (DA) resulting in an orange yellow colored DA-Mo(VI) complex. FT-IR was used to characterize complex formation between DA and AM via hydrogen bonding or electrostatic interactions. [Figure S1 ESI†]. The Mo(VI)@PDA was pyrolyzed at 1000°C under Ar in presence of elemental sulfur to yield MoS$_2$[@S$_x$-PDA].

From the FESEM images (Figure 1a) of MoS$_2$ and MoS$_2$[@S$_x$-PDA], it is evident that MoS$_2$ is mainly made of both particles and sheets whereas, the MoS$_2$[@S$_x$-PDA] has sheets stacked together. We further investigated the morphology by using TEM. Figure 1b shows the TEM images of MoS$_2$ and MoS$_2$[@S$_x$-PDA] that are in agreement with FESEM images of MoS$_2$ displaying particulate morphology with an average particle size of ~100 nm whereas, MoS$_2$[@S$_x$-PDA] shows a few or more wrinkled sheets. In order to assess the crystal structure X-ray diffraction (XRD) measurements were performed. Figure 2a compares the diffraction patterns of MoS$_2$ and MoS$_2$[@S$_x$-PDA]. The XRD pattern of MoS$_2$ shows crystalline reflections at 14.49 (002), 32.97 (101), 39.90 (103), 49.58 (105) and 60.70 (111) and MoO$_3$ at 26.21 (021), 37.16 (131), 53.77 (080), 66.70 (270). On the other hand, MoS$_2$[@S$_x$-PDA] displays a nominal shift of the reflection at 14.49 (002) towards lower angles indicating an increase in the interlayer spacing from 6.14 to 6.41 Å due to layer expansion and the presence of defects in MoS$_2$ sheets. Also, MoS$_2$[@S$_x$-PDA] was...
found to be nanocrystalline with considerable increase in fwhm compared to its native counterpart.

Figure 1: FESEM and TEM images of (a) MoS\(_2\) and (b) MoS\(_2\)@S-C-PDA [Scale bars for TEM: (a) 200 nm; (b) 50 nm]

The stack height along the c-axis was estimated for MoS\(_2\) and MoS\(_2\)@S-C-PDA using Scherrer equation and found to be 25 and 16.7 nm respectively indicating that MoS\(_2\) exists as a few layers in MoS\(_2\)@S-C-PDA.\(^{36}\) As expected, sulfide PDA-derived carbon (S-C-PDA) is found to be nanocrystalline with its characteristic peak at 25° (Figure S2 ESI†). To confirm the presence of carbon and defects, Raman spectra were acquired for MoS\(_2\) and MoS\(_2\)@S-C-PDA (Figure 2b). As expected both the spectra show well-defined peaks of MoS\(_2\) at 410 and 384 cm\(^{-1}\) attributed to A\(_{1g}\) and E\(_{2g}\) bands respectively. In addition to the characteristic MoS\(_2\) peaks, MoS\(_2\)@S-C-PDA displayed D and G bands at 1384 and 1560 cm\(^{-1}\) ascribed to the presence of carbon formed from PDA (Figure S3 ESI†). A minimal decrease in \(\Delta \nu\) of A\(_{1g}\) and E\(_{2g}\) in MoS\(_2\)@S-C-PDA (25 cm\(^{-1}\)) compared to MoS\(_2\) (28 cm\(^{-1}\)) suggests that MoS\(_2\) exists as sheets in MoS\(_2\)@S-C-PDA.\(^{37}\) A low intense and broad E\(_{2g}\) band of MoS\(_2\)@S-C-PDA compared to MoS\(_2\) indicates defects arising from the presence of unsaturated sulfur at the edge planes.\(^{38,39}\)

The oxidation state and elemental analysis were carried out using X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum of MoS\(_2\) shows C, O, Mo, S peaks at the corresponding binding energies. The high resolution carbon spectrum of MoS\(_2\)@S-C-PDA (Figure S3a) shows peaks at 284.37, 285.20 eV corresponding to C=C, C-C or C-H indicative of the presence of sp\(^{2}\) and sp\(^{3}\) carbon respectively. While a broad peak at 288.56 eV corresponds to the presence of O=C-O species, the additional peak observed at 286.19 eV arises due to the sulfur-bound carbon (C-S).\(^{40,41}\) Furthermore in S_2P spectra, the peak at 163.9 eV is 2p\(_{3/2}\) of thiophene-S due to spin-orbit coupling and the peak at 168.0 eV is the oxide-bound sulfur species (C-SO\(_2\)-C) confirming sulfur-doping in the PDA-derived carbon.\(^{42}\) Further, FT-IR was used to confirm S-doping of the carbon matrix (Figure S4 ESI†). Both MoS\(_2\)@S-C-PDA and MoS\(_2\) samples display their characteristic v (Mo-S) peak at 462 cm\(^{-1}\). Additionally, the appearance of new peaks at 902 and 1110 cm\(^{-1}\) attributed to \(\delta(C-S)\) and \(\delta(C=S)\) respectively in the MoS\(_2\)@S-C-PDA spectra is a clear confirmation of attachment of sulfur to the carbon skeleton. FTIR spectra of S-doped carbon also show peaks of \(\delta(C-S)\) and \(\delta(C=S)\) similar to MoS\(_2\)@S-C-PDA.\(^{43}\)

Deconvoluted Mo peak of MoS\(_2\) sample shows that Mo is in (IV) oxidation state with binding energies of 229.30, 232.45 eV corresponding to 3d\(_{3/2}\), 3d\(_{5/2}\) respectively. The peak located at 235.0 eV can be attributed to the presence of Mo-O bond with Mo (VI) oxidation state.\(^{43,44}\) Deconvoluted sulfur peak shows a doublet at 161.55 eV for S_2P\(_{3/2}\) and 162.77 eV for S_2P\(_{1/2}\) confirming the presence of sulfide species, S\(_2\) (Figure S5 ESI†). The stoichiometric ratio of Mo:S in MoS\(_2\) and MoS\(_2\)@S-C-PDA samples is found to be ~2. Interestingly, in MoS\(_2\)@S-C-PDA, a shift of 0.6 eV is observed in the binding energies of Mo (228.71 and 231.79 eV) and S (161.55, 162.77 eV). The shift in the binding energies implies the emergence of both 1T- and 2H-phases owing to the incorporation of S-doped carbon between the MoS\(_2\) sheets resulting in layer expansion, as is also evident from an increase in the interlayer spacing (Figure 2a).\(^{21,44}\) From the structural and chemical evaluation of MoS\(_2\)@S-C-PDA, it is reasonable to conclude that S-doped carbon is incorporated between MoS\(_2\) sheets resulting in the transformation of 2H (semiconducting) to 1T phase (metallic) with more unsaturated sulfur atoms at the edges thereby increasing the number of active sites, for instance in electrocatalysis. Besides, structural modification and electronic modulation are known to play vital roles in the design of electrocatalysts.

Figure 2: (a) XRD and (b) Raman spectra of MoS\(_2\) and MoS\(_2\)@S-C-PDA

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Figure 3: High resolution x-ray photoelectron spectra of (a) C, and (b) Mo\(_{3d}\) in MoS\(_2\)@S-C-PDA

Incorporation of heteroatoms between the MoS\(_2\) nano-sheets in a controlled manner results in increased intrinsic conductivity and charge density.\(^{45,36}\) Analogously, the band gaps of MoS\(_2\) and MoS\(_2\)@S-C-PDA were determined using diffuse reflectance spectroscopy (DRS) to be 1.32 (indirect) and ~1.68 eV (direct) respectively (Figure S6). Bulk MoS\(_2\) is well-known to show an indirect band gap of ~1.2 eV and single layer MoS\(_2\) displays a direct band gap of ~1.8 eV.\(^{46}\) It has been predicted that double and triple layers of MoS\(_2\) show reduced band gap values of ~1.65 and 1.35 eV relative to a single layer MoS\(_2\) suggesting that MoS\(_2\)@S-C-PDA consists of two layers (Figure S6 ESI†).\(^{47}\) Furthermore, the band gap transition is well supported by UV-visible spectra (Figure S7 ESI†). Absorption spectra of MoS\(_2\) and MoS\(_2\)@S-C-PDA display A and B
excitonic bands at 634 (1.95 eV), 687 nm (1.80 eV) respectively, corresponding to K and K’ of the Brillouin zone. In addition to K and K’ bands, a broad peak at ~400 nm with two shoulder peaks at 398 and 448 nm were observed for MoS\textsubscript{2}@S-C\textsubscript{PDA} which can be ascribed to the direct transition of deep valence band to the conduction band.\textsuperscript{45} A blue shift in A and B exciton bands in MoS\textsubscript{2}@S-C\textsubscript{PDA} can be attributed to the quantum-size confinement. Overall, the incorporation of S-doped carbon between MoS\textsubscript{2} sheets results in structural and electronic modification which is expected to favour enhancement in the hydrogen evolution reaction kinetics.

In order to evaluate the electrocatalytic activity of MoS\textsubscript{2}@S-C\textsubscript{PDA}, HER was performed in 0.5 M H\textsubscript{2}SO\textsubscript{4} solutions using linear sweep voltammetry with a conventional 3-electrode setup. Figure 4a compares the linear sweep voltammograms of S-C\textsubscript{PDA}/GC, MoS\textsubscript{2}/GC, MoS\textsubscript{2}@S-C\textsubscript{PDA}/GC electrodes and benchmark Pt. MoS\textsubscript{2}/GC and S-C\textsubscript{PDA}/GC are active to HER at higher overpotentials (η > 300 mV), whereas MoS\textsubscript{2}@S-C\textsubscript{PDA}/GC shows onset of catalytic current at 60 mV vs RHE. As in the case of other MoS\textsubscript{2}-based electrocatalysts, the present system is relatively closer to the performance of Pt in terms of proximity of the onset potential. The Tafel slopes determined from the linear region of the polarization curve is either followed by surface atom (Tafel reaction) or ion-atom reaction (Volmer reaction). The second step is either followed by surface atom (Tafel reaction) or ion-atom recombination (Heyrovsky reaction).\textsuperscript{39} If the Tafel slope is 30 mV/decade, HER takes place via Volmer-Tafel or if it is above 40 mV/decade, it follows Volmer-Heyrovsky mechanism. In the present work, the HER on MoS\textsubscript{2}@S-C\textsubscript{PDA} shows a Tafel slope of 72 mV/decade suggesting Volmer-Heyrovsky mechanism. Similarly, the exchange current density (j\textsubscript{0}) calculated for MoS\textsubscript{2}@S-C\textsubscript{PDA} is found to be 3.16×10\textsuperscript{-4} Acm\textsuperscript{-2} whereas, MoS\textsubscript{2} exhibited a value of 5.52×10\textsuperscript{-5} Acm\textsuperscript{-2} suggesting the presence of more active sites due to the presence of unsaturated sulfur atoms at the edge planes.

![Figure 4](image.png)

**Figure 4:** (a) Linear sweep voltammograms of MoS\textsubscript{2}@S-C\textsubscript{PDA}, MoS\textsubscript{2} and S-C\textsubscript{PDA} modified electrodes in 0.5M H\textsubscript{2}SO\textsubscript{4} (scan rate 2 mV/sec)(b) Impedance spectra of MoS\textsubscript{2}@S-C\textsubscript{PDA} and MoS\textsubscript{2} samples at overpotential of 150 mV. Electrolyte: 0.5M H\textsubscript{2}SO\textsubscript{4}, Frequency range: 1MHz-50 mHz. Amplitude: 10 mV

Additionally, the current density measured at a constant overpotential of 200 mV for MoS\textsubscript{2}@S-C\textsubscript{PDA} shows 18-fold increase (20 mA cm\textsuperscript{-2}) compared to MoS\textsubscript{2} (0.7 mA cm\textsuperscript{-2}). It is evident from Table 1 that HER activity in terms of onset potential and exchange current density is superior to that of the other carbon-supported MoS\textsubscript{2} nano-sheets.\textsuperscript{13-15, 35} In support of this observation, higher exchange current density and current density calculated at a constant overpotential indicates superior electrocatalytic activity of MoS\textsubscript{2}@S-C\textsubscript{PDA} relative to its counterparts. At the same time, it needs to be noted that MoS\textsubscript{2}@S-C\textsubscript{PDA} exhibits a lower current density at 200 mV relative to other carbon-supported systems which may be due to: (i) lower conductivity of PDA-derived carbon compared to the graphene substrates; (ii) limited electron conduction compared to the graphene substrates [2]; and (iii) surface area of the PDA-derived carbon being lower than the nanoscopic graphene sheets.

Furthermore, to elucidate charge transport, interfacial charge transfer resistance (R\textsubscript{ct}) values for MoS\textsubscript{2}@S-C\textsubscript{PDA}, MoS\textsubscript{2} are measured using electrochemical impedance spectroscopy at an overpotential of 150 mV (Figure 4b). The MoS\textsubscript{2}@S-C\textsubscript{PDA} and MoS\textsubscript{2} electrode shows R\textsubscript{ct} values of 900 Ω and 8 kΩ respectively. Significant decrease in R\textsubscript{ct} of MoS\textsubscript{2}@S-C\textsubscript{PDA} can be reasoned to the incorporation of sulfur-doped carbon aiding efficient charge transport. Stability of the electrode materials is one of the key parameters in determining the efficiency of electrocatalysts. Cyclic voltammetric experiments were performed in the potential range between the -0.3 to 0.2 V in acidic medium to evaluate the catalyst stability (Figure S8 ES\textsuperscript{†}). Even after 1000 cycles MoS\textsubscript{2}@S-C\textsubscript{PDA} electrode is able to retain its catalytic activity with a negligible decrease in the cathodic current.

Mechanistically, enhancement in the electrocatalytic activity may involve interplay of factors such as: (a) insertion of sulfur doped carbon between MoS\textsubscript{2} layers results in the MoS\textsubscript{2} structural rearrangements like layer expansion (confirmed by the d-spacing values in XRD) and also aids the 2H-1T phase transformation (as confirmed by XPS data). These studies reveal that MoS\textsubscript{2}@S-C\textsubscript{PDA} is enriched with unsaturated sulfur atoms at the edge sites; (b) this also brings about increased intrinsic electronic conductivity of MoS\textsubscript{2} nano-sheets that is reflected in the band gap changes. These structural and electronic rearrangements are in agreement with the previously reported density functional theoretical calculations performed on superlattices composed of graphene and MoS\textsubscript{2} layers\textsuperscript{50} and (c) MoS\textsubscript{2}@S-C\textsubscript{PDA} exhibits metallic character due to increased charge transport between atomic layers, indicating a weak ionic interaction between the sulfur doped carbon and the MoS\textsubscript{2} layers similar to van der Waals forces. This can be attributed to high charge density of the sulfur doped carbon, contributing to increased electronic conductivity. It is well known that electronic modification along with the creation of more defective or edge sites is beneficial to the enhanced HER electrocatalysis.

In conclusion, a simple two step synthetic protocol is developed by immobilizing PDA on Mo precursor through complexation followed by pyrolysis in presence of elemental sulfur yielding alternate layers of S-doped carbon and MoS\textsubscript{2} nano-sheets. Incorporation of S-doped carbon between MoS\textsubscript{2} nano-sheets leads to layer expansion resulting in structural and electronic modifications. The key factors such as the number of active sites (unsaturated sulfur atoms at the edge planes) and electrical conductivity required for HER are simultaneously achieved by incorporation of S-doped carbon. The MoS\textsubscript{2}@S-C\textsubscript{PDA} displayed HER activity with a minimal, onset potential of 60 mV vs. RHE with η = 160 mV@10 mA cm\textsuperscript{-2}. With this promising feature in mind, one may apply the present approach to other chalcogenides and compositional variations in order to achieve optimized catalytic performance. Further reduction in overpotential and enhancement in the current density may be possible by controlling the thickness of the doped carbon layers and in turn the electronic conductivity.
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[Electronic supplementary information are available: Chemicals, experimental procedure, characterization such as FTIR, XRD, XPS, Laser Raman, DRS, UV-visible and comparison table data. See DOI: 10.1039/c000000x]