Electronic Supporting Information (ESI)

Covalently conjugated MoS$_2$/Fe$_3$O$_4$ magnetic nanocomposite for efficient & reusable catalyst for H$_2$ production

Manish K. Jaiswal$^{\text{a,c}}$, *, Uttam Gupta$^{\text{a,b}}$, and Pratap Vishnoi

Authors contributed equally.
*Correspondence to: manish@jncasr.ac.in
Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore-560064, India

Experimental:

Chemical exfoliation of MoS$_2$ nanosheets (ce-MoS$_2$):

Bulk MoS$_2$ is composed of atomically-thin S-Mo-S sheets held together by weak van der Waals forces. The bulk MoS$_2$ was chemically exfoliated down to few layers using standard protocol reported elsewhere$^{[1]}$. In brief, 200 mg of MoS$_2$ (procured from Alfa Aesar) was degassed for an hour before adding 3 mL n-butyllithium (1.6 M in hexane, procured from Avra Laboratory, India) under N$_2$ atmosphere and then heated at reflux for 48h with continuous stirring. The reaction mixture was cooled to room temperature and added with 20 mL dried hexane and filtered with nylon paper (pore size~0.45µm). The excess n-butyllithium was washed with fry petroleum ether. The solid black precipitate was dispersed in 200 mL of deionized water in a round-bottom flask and sonicated for an hour in an ice-cold water-bath assist the exfoliation. To remove partially stacked layers from the suspension, the solution was centrifuged at 2x5000 rpm for 10 min each cycle followed by 2x8000 rpm for another 10 min each cycle. The dispersion was collected and used for further experiments. The concentration of the aqueous dispersion of MoS$_2$ was 40 ppm, determined by ICP.

Surface modification of ce-MoS$_2$:

The exfoliated nanosheets of MoS$_2$ were functionalized with carboxylate groups using reported method with slight modification$^{[1-2]}$. 100 mL aqueous dispersion of ce-MoS$_2$ was added with 5-fold excess of bromoacetic acid in 20 mL 2-propanol and stirred for 48 h. The black precipitate was collected, washed with ethanol and dried.

Amine functionalized-Fe$_3$O$_4$ nanoparticle (NP) synthesis:

2 g of FeCl$_2$.4H$_2$O and 5.4 g of FeCl$_3$.6H$_2$O (Sigma, USA) were mixed in 30 mL ethylene glycol and the solution was stirred at 70 °C under N$_2$ atmosphere for 1h. 2g of sodium acetate was added to the above mixture and the mixture was further stirred for 30 min. Subsequently 10 mL of
ethylenediamine (EDA) was added and the reaction was reflux at 270 °C for 6 h. The reaction was cooled down to room temperature and the black precipitate was collected \[3\]. The obtained sample was then washed three times with water to remove unreacted reagents. In such method, the one end amine groups from EDA co-ordinates with Fe-O from the nanoparticle surface and other end remain extended in water to provide the nanoparticle aqueous stability.

**Covalent conjugation of Amine-Fe$_3$O$_4$ NPs onto ce-MoS$_2$ nanosheets:**

Conjugation of Fe$_3$O$_4$ NP to ce-MoS$_2$ nanosheets in 1:1 (Mo:Fe) atomic ratio was carried out via amine-carboxylate interaction using DCC (N,N’-dicyclohexylcarbodiimide) coupling reaction in presence of dried DCM (dichloromethane) solvent. In typical reaction system, 68 mg of NPs was mixed with 20 mg of surface modified ce-MoS$_2$ along with 235 mg of DCC. The mixture was degassed before 20 mL of dried DCM was added into the flask and stirred for 24h. The sample was washed with ethanol three times to remove unreacted reagents and dried powder was stored for further experiments. Following the method, other ratios of MoS$_2$/Fe$_3$O$_4$ such as 1:5, 5:1, and 1:10 were also prepared.

**Pt-grafting to Fe$_3$O$_4$ & MoS$_2$/Fe$_3$O$_4$ nanocomposite:**

10 mg of the MoS$_2$/Fe$_3$O$_4$ nanocomposite was mixed with 78 µL of Pt solution (aqueous H$_2$PtCl$_6$ 8.85 mM, equivalent of 1 wt.% Pt) in 10 mL ethanol. The mixture was exposed to UV-radiation for 2h for uniform adhesion of Pt onto nanocomposites surfaces.

**Photocatalytic water-splitting HER:**

5 mg of the sample was taken and dispersed in 15% v/v triethanolamine solution. Prior to H$_2$ evolution studies, the solution was thoroughly purged with N$_2$ and 14 µM of dye was added to it. The solution was then illuminated with 100 W halogen lamp. The evolved H$_2$ gas was analyzed with a Thermal Conductivity Detector (TCD) equipped gas chromatograph at regular intervals.

**Materials characterizations:**

The phase confirmation of Fe$_3$O$_4$ NP was carried out by powder X-ray diffraction using copper K$_{α}$ source (1.54 Å) on a Bruker D8 diffractometer. The surface modification of MoS$_2$ nanosheets with carboxylate and their further covalent conjugation with amine-functionalized NPs were confirmed with FT-IR using KBr pellet as sample matrix. The TEM images of the nanoparticles and the composite samples were taken with JEOL JEM 2010 operated at 300 keV.

The functionalization data was further corroborated with X-ray photoelectron spectra (XPS) recorded for Mo (3d), S (2p), and C (1s) core level electron’s binding energies. The data were recorded with Omicron XPS equipped with Argus detector and analyzed with Fityk software. The change in two prominent Raman characteristic phonon modes, E$_{12g}$ and A$_{2g}$ of 2D MoS$_2$ were recorded after exciting the samples by 532 nm green laser (Horiba Inc.). The UV absorbance and
photoluminescence characters of nanocomposite samples were studied in solution by UV-Vis spectrophotometer (Shimadzu Scientific Instruments). The individual contribution of constituents in the nanocomposites were determined by thermogravimetric analysis, TGA (STRA-TGA instrument Mettler-Toledo) by running the solid powder samples from room temperature to 800 °C under nitrogen atmosphere. All the magnetic measurements were carried out by SQUID in powder form. The FE-SEM images along with elemental EDS (Energy dispersive X-ray spectroscopy) mapping of the nanocomposite was taken with FEI Quanta 600 operated at 15 keV.
X-ray powder diffraction (XRD):

Figure S1: Powder X-ray diffraction pattern of amine functionalized iron oxide NPs (EDA- Fe$_3$O$_4$) confirms the formation of magnetite phase (JCPDS card no. 19-0629). The crystallite size, using Scherrer equation, was calculated to be approx. 20 nm.
FT-IR spectra:

**Figure S2**: FT-IR spectra of EDA-Fe$_3$O$_4$ NPs and covalently conjugated MoS$_2$/Fe$_3$O$_4$ nanocomposite. Amine stretching (-NH$_2$ str.) obtained at 3415 cm$^{-1}$ confirmed the functionalization of NP by ethylenediamine. The -OH and alkane (-CH, -CH$_2$) stretching vibrations in the nanocomposites appear at 3325, 2930 and 2850 cm$^{-1}$ respectively.
X-ray Photoelectron spectra (XPS):

The very presence of binding energy (BE) peaks for Mo$^{4+}$ doublets, $3d_{5/2}$ at 228.3 and $3d_{1/2}$ 231.6 eV and of S$^{2-}$ doublets, $2p_{3/2}$ at 161.2 and $2p_{1/2}$ at 162.7 eV confirmed the dominant 1T-phase. However, the trace occurrence of 2H phase was well observed as the high energy bands for both Mo$^{4+}$ ($3d_{5/2}$, 228.9 eV and $3d_{3/2}$, 232.4 eV and therefore $\Delta=1.5$ eV) and S$^{2-}$ ($2p_{3/2}$, 162.3 eV and $2p_{1/2}$, 164.2 eV) belonging to trigonal prismatic co-ordination of molybdenum with sulfur atoms were present in the spectra. The arithmetical area under the curve suggests the ratio of 2H and 1T phases in the ce-MoS$_2$ is approx. 35:65.

The conjugation with NP via amide linkages was further corroborated using XPS by analyzing changes in the binding energies (BE) of core level electron of C 1s of carboxyl functionalized MoS$_2$ and nanocomposite (MoS$_2$-Fe$_3$O$_4$) spectra (Fig. S2b). While the BE for C-C ($sp^2$) hybridized orbitals appears at 284.5 eV, the signals for C=O and HO-C=O functional groups in carboxyl-MoS$_2$ were observed at 286.6 and 288.3 eV respectively. Due to covalent conjugation with amine-Fe$_3$O$_4$, there was considerable reduction in the BE for $sp^2$ (284.2 eV) and C=O (285.8 eV) due to amide linkage. Further, the formation of RN-C=O gave rise to signal at 287.7 eV while the BE for carbon-sulfur (C-S) due to MoS$_2$-CH$_2$COOH (285.5 eV) shifted to lower energy band (285.0 eV).

**Figure S3**: XPS was used to corroborate (a) the phase of ce-MoS$_2$ and (b,c) covalent conjugation to the NPs.
Raman spectra for the nanocomposites samples were analyzed to confirm the covalent conjugation of the surface modified \textit{ce}-MoS$_2$ nanosheets with nanoparticles (Figure S3). The characteristic peaks for bulk MoS$_2$, $E_{1g}$ (in-plane vibrations) and $A_{1g}$ (out-of-plane vibrations) appear at 403.5 and 378.1 cm$^{-1}$ respectively. The modification of \textit{ce}-MoS$_2$ sheets with carboxylate groups shifted these peaks to the lower frequencies. Due to additional ligands conjugated to the MoS$_2$ lattice their vibrational frequencies have attenuated and therefore softening. Further the conjugation of the NP to the MoS$_2$ sheets via amide linkages causes further changes in the vibrational frequencies. It is worth noting that the characteristic $E_{1g}$ signifies to the lattice strain while $A_{2g}$ correlates with the van der Waals interaction between layers. Due to the nanoparticles conjugation to the \textit{ce}-MoS$_2$ sheet, the obtained blue shifts indicate enhanced lattice stiffness and high inter-layer interaction.

\textbf{Figure S4.} Raman spectra of \textit{ce}-MoS$_2$ and the nanocomposite illustrating changes in the characteristic vibrational $E_{1g}$ and $A_{2g}$ modes
Photoluminescence:

![UV-visible absorbance](image1)

![Photoluminescence](image2)

**Figure S5.** Photoluminescence (PL) of nanocomposite (MoS$_2$/Fe$_3$O$_4$). (a) The UV spectrum shows absorbance profile of the sample (b) PL signal from the nanocomposite.

The PL character of MoS$_2$ are uniquely associated with its atomically thin-layered nanostructure. The bulk MoS$_2$ is an indirect band gap (~1.2 eV) semiconductor, and shows weak PL signal. However, when it is reduced to few layers to monolayer, it turns into direct band gap (~1.9 eV) semiconductor and generates strong PL spectrum$^5$. The covalent conjugation of NP onto the MoS$_2$ sheet did not inhibit its photoluminescence. A typical UV-visible spectral profile for MoS$_2$/Fe$_3$O$_4$ (1:1) exhibits the characteristic absorbance for the composite at around 470 to 500 nm (Fig. S3a). The sample was therefore chosen to excite at 488 nm which yielded in an intense PL band at approx. 735 nm indicating the potential use of the composite in water-splitting experiments for hydrogen evolution (Fig. S4b).
**Thermogravimetric analysis:**

![Thermogravimetric analysis](Image)

**Figure S6:** Thermogravimetric weight loss for nanocomposites along with amine-functionalized Fe$_3$O$_4$ nanoparticles. The weight percentage for EDA was 8% of the total nanoparticle weight, while for surface modification with bromoacetic acid accounted for about 10% weight in MoS$_2$. When the composition was made in 1:1 atomic ratio of Mo:Fe, the weight loss accounted for about 75% which reduced the magnetization from 49.3 to 8 emu.g$^{-1}$ at 50kOe (Figure 2, main text).
TGA & Magnetic measurements for more compositions:

**Figure S7:** (a) The thermogravimetric curves for MoS$_2$/Fe$_3$O$_4$ nanocomposites (1:5 and 5:1 atomic ratios of Mo:Fe) along with their (b,c) magnetic measurements. The magnetization values were approx. 11.9 and 15.1 emu.g$^{-1}$ at 50 kOe and associated weight loss attributed to the non-magnetic contents were 68% and 55% respectively. Interestingly the covalent conjugation with 2D-MoS$_2$ sheets did not alter magnetic character of magnetite phase and all compositions showed superparamagnetic behavior.

We further analyzed the FC/ZFC (zero field-cooled and field-cooled) behaviors of the samples (Figure S6c). Amine-functionalized magnetite showed the blocking temperature at about 380K (Fig. 2b, manuscript) and for nanocomposite (1:1), the two curves come closure at about 200K and continued in parallel. Similar trend was observed for other compositions; 1:5 and 5:1 where the ZFC/FC curves tend to meet at about 300K, which is mainly due to the particle-sheet interactions. This again proves the chemical binding among 2D MoS$_2$ nanosheets and 0D Fe$_3$O$_4$ nanoparticles. These results further indicated that increasing the atomic ratio for Mo with respect to Fe, imparts higher degree of chemical interactions and thus may lower down the blocking temperature.
Figure S8: (a) SEM micrograph and elemental confirmation in the nanocomposites (MoS$_2$/Fe$_3$O$_4$). (b) The presence of Mo ($L_\alpha=2.29$ keV), S ($K_\alpha=2.3$ KeV), Fe ($K_\alpha=6.4$, $K_\beta=7.05$ KeV), O ($K_\alpha=0.5$ KeV) and Pt ($M_\alpha=2.05$ keV) in the nanocomposite (1:1) was confirmed by energy-dispersive X-ray spectra (EDS).
HR-TEM of nanocomposite:

**Figure S9:** High-resolution TEM image of the nanocomposite (1:1) incorporated with 1% Platinum. The image shows the presence of lattice fringes corresponding to Fe$_3$O$_4$ NP and Pt in the nanocomposite. The inset image reveals the presence of nanoparticles together with Pt nanoparticles grafted with the MoS$_2$ sheets.
**BET Surface analysis:**

![BET Surface analysis graph](image)

**Figure S10:** BET surface analysis of the samples. The adsorption-desorption curve for nanocomposite together with EDA-Fe$_3$O$_4$ and MoS$_2$-CH$_2$COOH show type IV isotherm. The calculated surfaces areas for the samples MoS$_2$-CH$_2$COOH, EDA-Fe$_3$O$_4$ and nanocomposites are approx. 72, 96 and 23 m$^2$/g respectively.
The course of hydrogen evolution was studied for Fe$_3$O$_4$ and its nanocomposites with MoS$_2$ (MoS$_2$/Fe$_3$O$_4$ in the ratio of 1:1, 1:5, and 1:10 respectively) for a period of 3h. The hydrogen evolution for EDA-Fe$_3$O$_4$ was measured to be approx. 60 µmoles h$^{-1}$g$^{-1}$ and while highest value was obtained for the composite (1:5) with the activity of about 310 µmoles h$^{-1}$g$^{-1}$. The other compositions 1:1 and 1:10 (data not shown) yielded maximum of ~120 and 60 µmoles h$^{-1}$g$^{-1}$ of H$_2$ respectively. Thus, we observed a significant five-fold enhancement in the catalytic activity of the Fe$_3$O$_4$ NPs when they were conjugated onto MoS$_2$ sheets in the ratio of 1:5. The low value of H$_2$ production using 1:10 ratio (data not shown) can be attributed to the low number of anchoring sites available onto the sheets to accommodate disproportionately large number of nanoparticles. Besides, it should also be noteworthy that Pt itself doesn’t induce any degree of H$_2$ production. Overall, the compositions showed higher activity than the nanoparticles, the amplitude of
enhancement was considerably better for 1:5 ratio which exhibited the optimal composition of MoS$_2$/Fe$_3$O$_4$ obtained for photochemical HER.

References: