Electronic Supplementary Information

Assemblies of Covalently Cross-linked Nanosheets of MoS_2 and of MoS_2-RGO: Synthesis and Novel Properties

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Experiemental section:

Reagents and precursors: Chemicals used in synthesis were of high purity and obtained from commercial sources. Solvents were pre dried before synthesis. 4,4′-diethynylbiphenyl (DEBP) was synthesized using previously reported procedure.[1]

Hydrogen evolution measurements:

MoS_2 and MoS_2-RGO assemblies were dispersed in a solution of water and triethanolamine (TEAO) (15% v/v) by sonication, to this 14 µmol of Eosin Y dye was added. The vessel was purged with N_2, and illuminated by 100 W halogen lamp under constant stirring. The evolved gases were manually collected from the headspace and analyzed in thermal conductivity detector (TCD) in a gas chromatograph (PerkinElmer Clarus ARNEL 580GC).

The turn over frequency (TOF) is calculated with respect to catalyst from formula,

$$TOF\ (/h) = \frac{moles\ of\ Hydrogen\ evovled\ per\ hour\ (activity\ of\ the\ catalyst)}{moles\ of\ the\ catalyst\ used}$$

Instrumentation:

Infrared (IR) spectra were recorded using Bruker ATR-FTIR spectrometer. Morphological analysis has been performed using Nova Nano SEM 600, FEI Company. Transmission Electron Microscopy (TEM) has been carried out with FEI TITAN3TM with an accelerating voltage of 80 kV. Thermo gravimetric analysis (TGA) was done in nitrogen atmosphere in the range of 30-900 ^{o}C at a heating rate of 3 ^{o}C/ min using Mettler Toledo TGA 850 instrument. XP spectra were recorded in an Omicron Nanotechnology Spectrometer with Mg K-α as the X-ray source. PXRD pattern of MoS_2 and MoS_2-RGO assemblies were recorded in PANanlytical Empyrean using Cu K-α radiation.

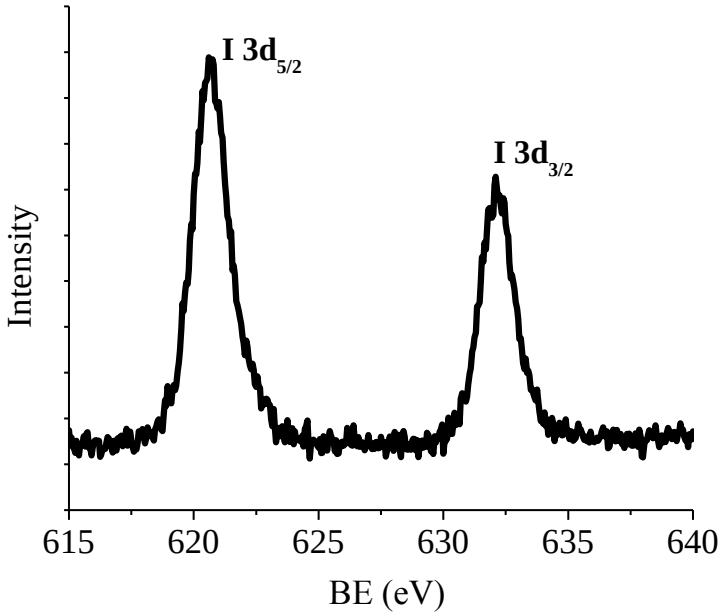

Fig. S1 High resolution Iodine (3d) X-ray photoelectron spectrum of Iodobenzene functionalized RGO.

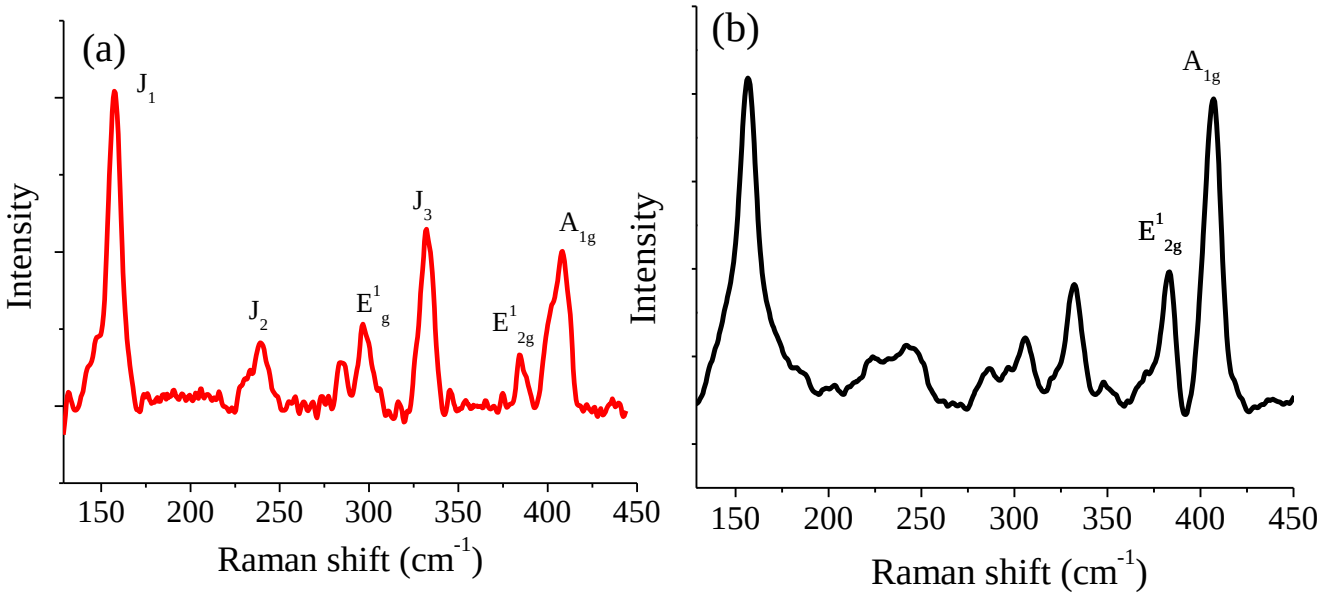

Fig. S2 Raman spectrum of (a) Exfoliated MoS_2 (red) and (b) Iodobenzene functionalized MoS_2 (black). (Raman spectrum of exfoliated MoS_2 is recorded in the as obtained liquid state).

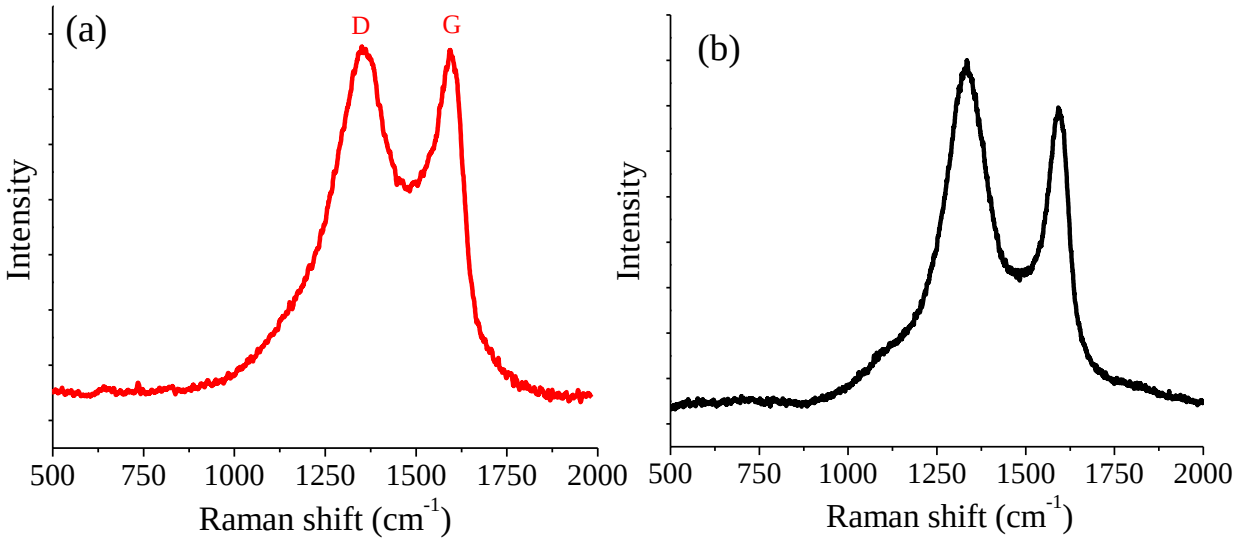

Fig. S3 Raman spectrum of (a) Reduced graphene oxide (red) and (b) Iodobenzene functionalized RGO (black).

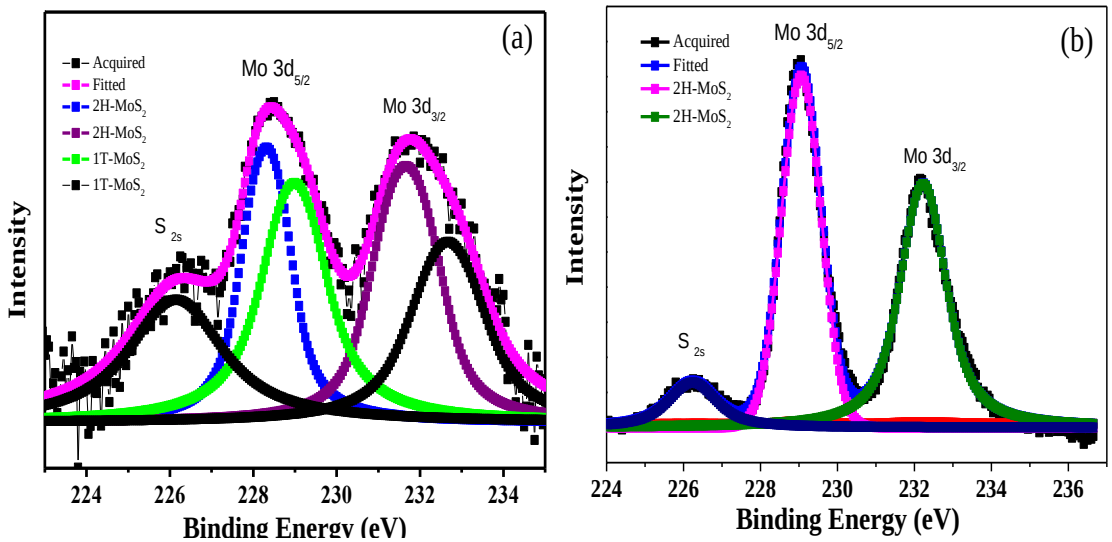

Fig. S4 Molybdenum (Mo) (3d) X-ray photoelectron spectrum of (a) Iodobenzene functionalized MoS_2 and (b) MoS_2 assemblies. (Mo (3d) peaks are deconvoluted to show 1T and 2H components).

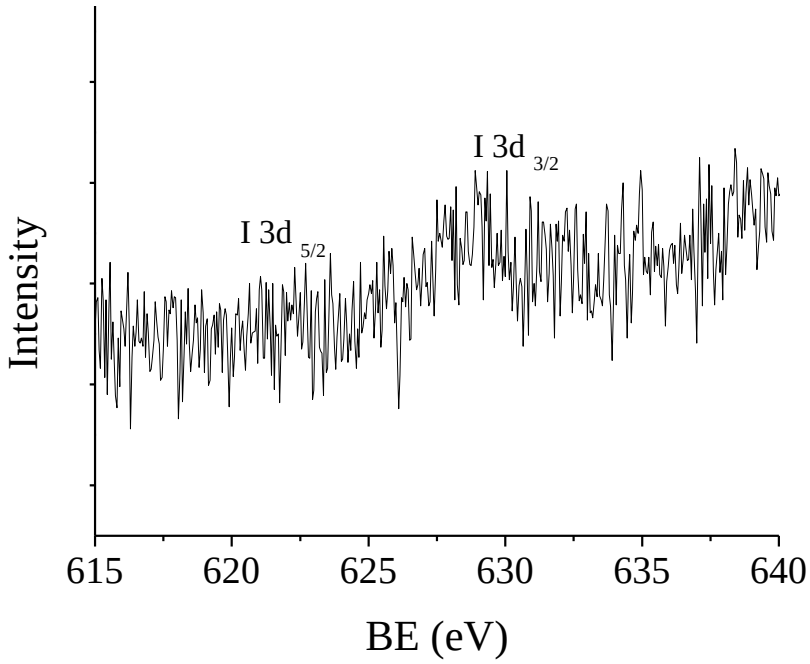

Fig. S5 Iodine (3d) X-ray photoelectron spectrum of MoS_2 assemblies.

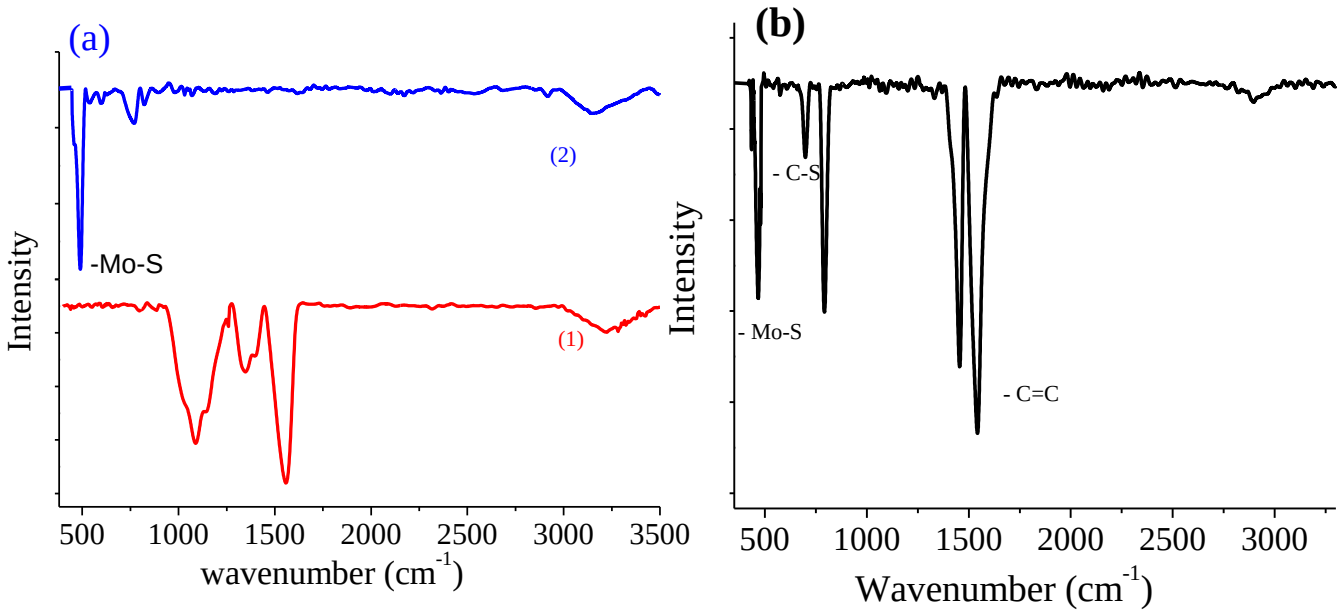

Fig. S6 (a) ATR-FTIR spectra of Reduced graphene oxide (1, red) and MoS_2 (2, blue); (b) Iodobenzene functionalized MoS_2.

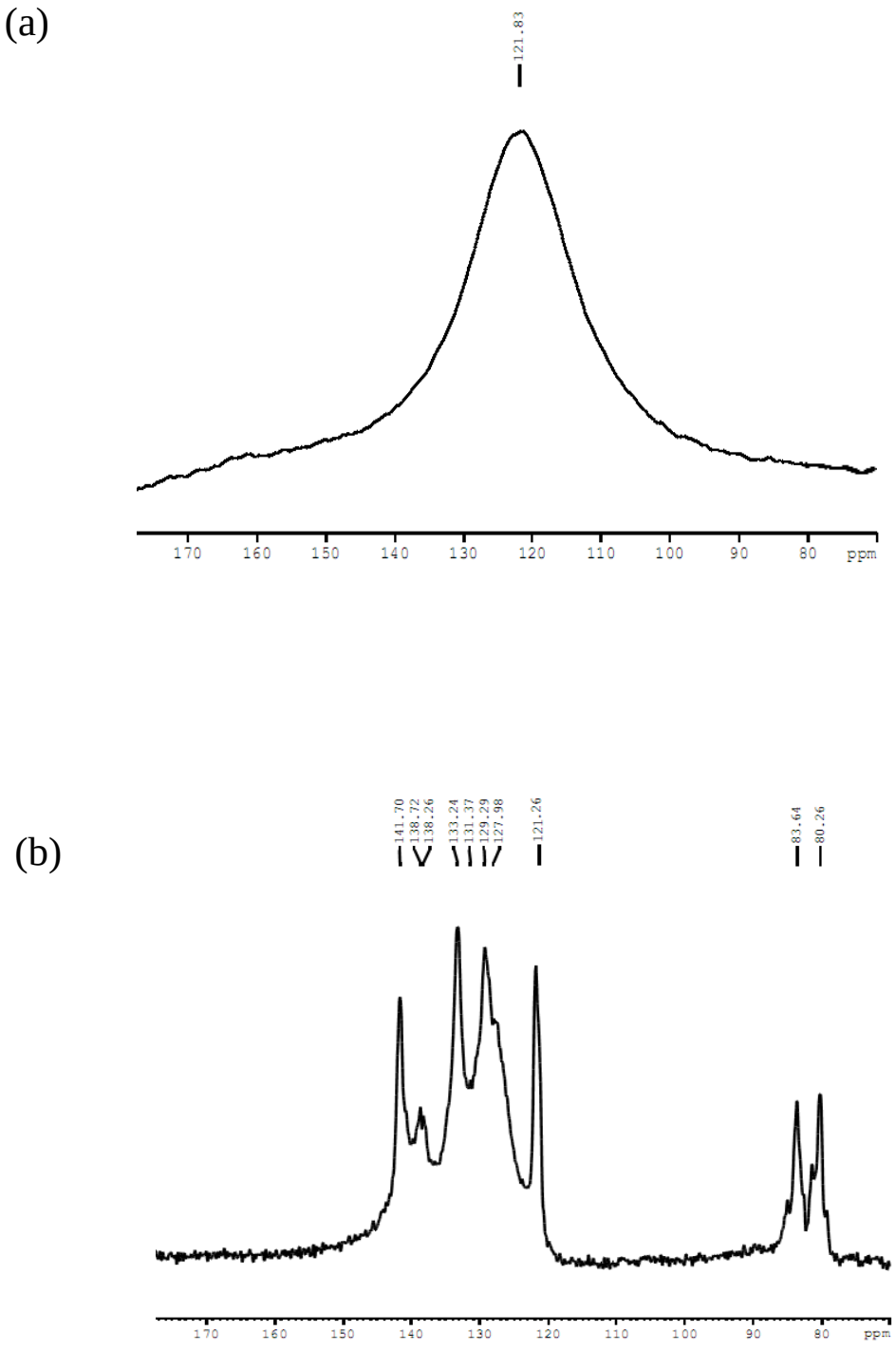

Fig. S7 ^{13}C MAS NMR spectrum of (a) RGO and (b) MoS_2-RGO assemblies at 11 kHz.

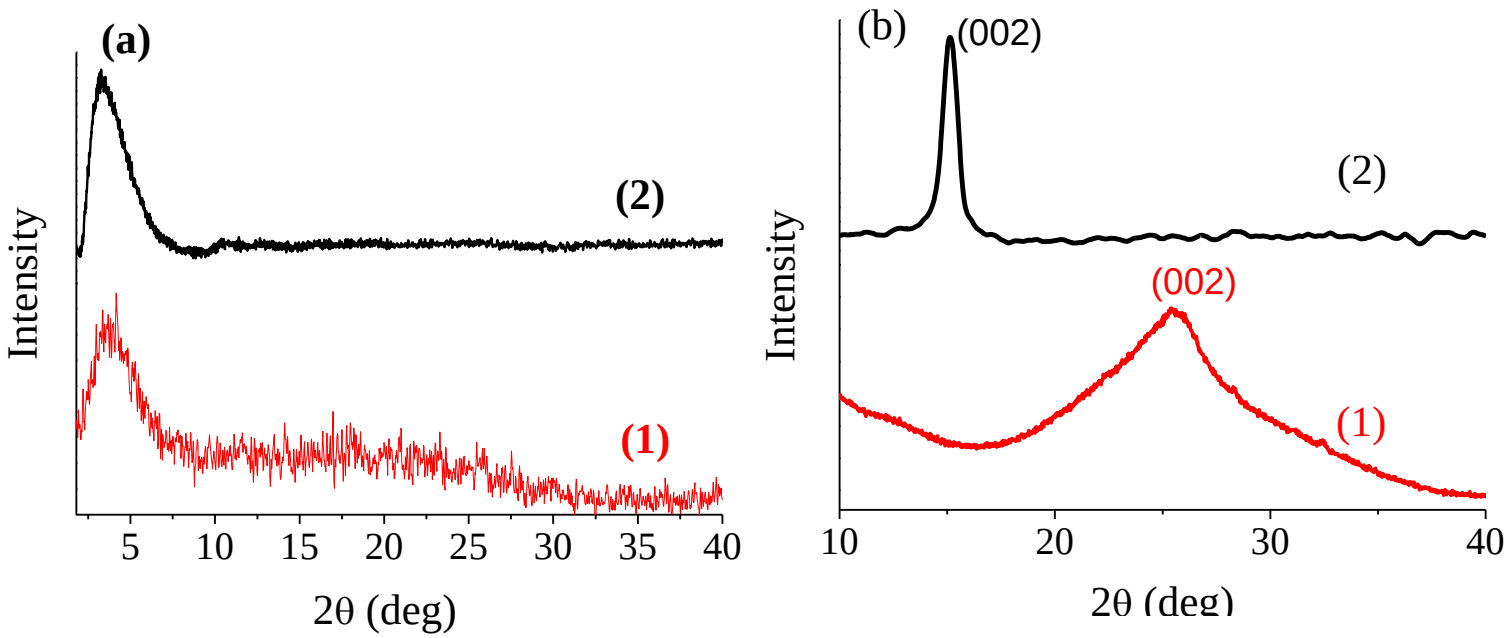

Fig. S8 PXRD pattern of (a) MoS_2-RGO assemblies (1, red) and MoS_2 assemblies (2, black); (b) RGO-IBz (1, red) and MoS_2-IBz (2, black).

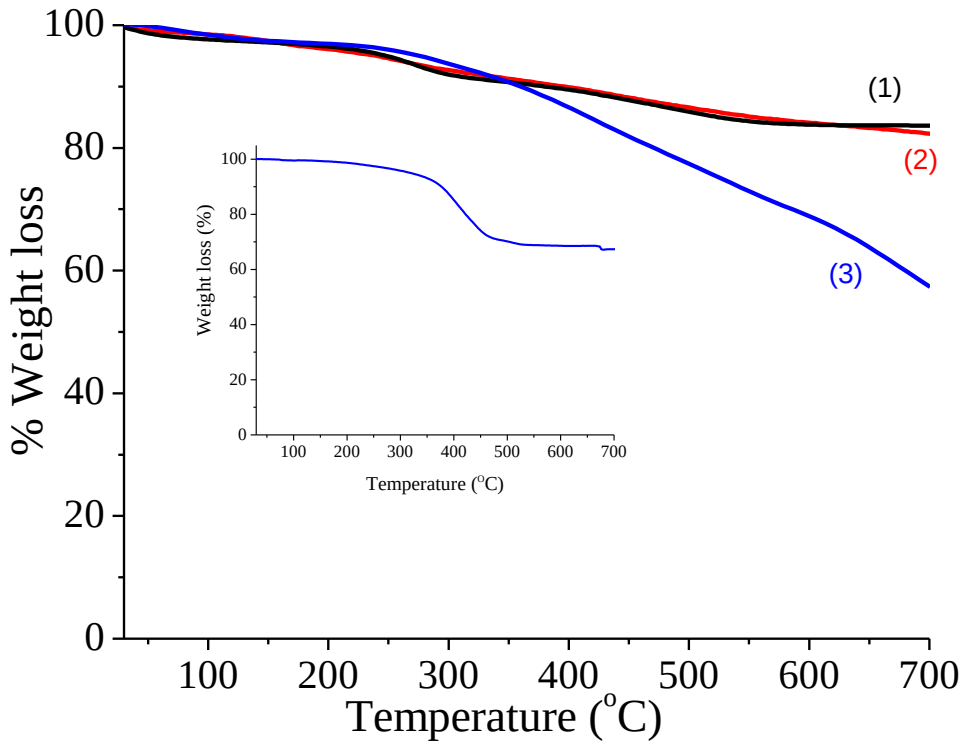

Fig. S9 TGA profile of MoS_2 assemblies (1, black), (2) MoS_2-RGO (2, red) assemblies and RGO (3, blue) (inset image shows TGA profile of MoS_2-IBZ).

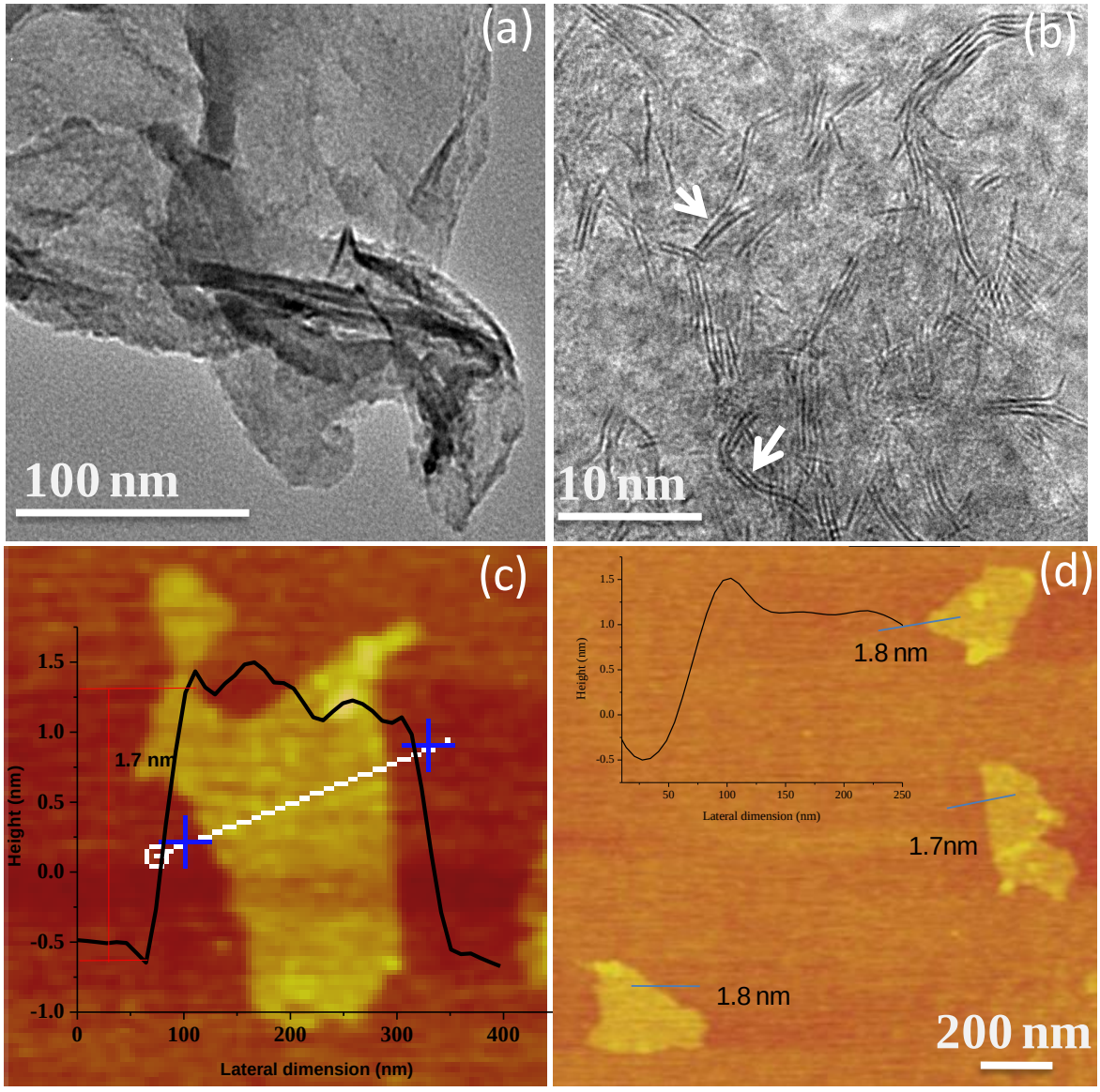

Fig. S10 (a) TEM, (b) HRTEM (arrows indicates (002) lattice fringes) and (c, d) AFM images of exfoliated MoS_2.

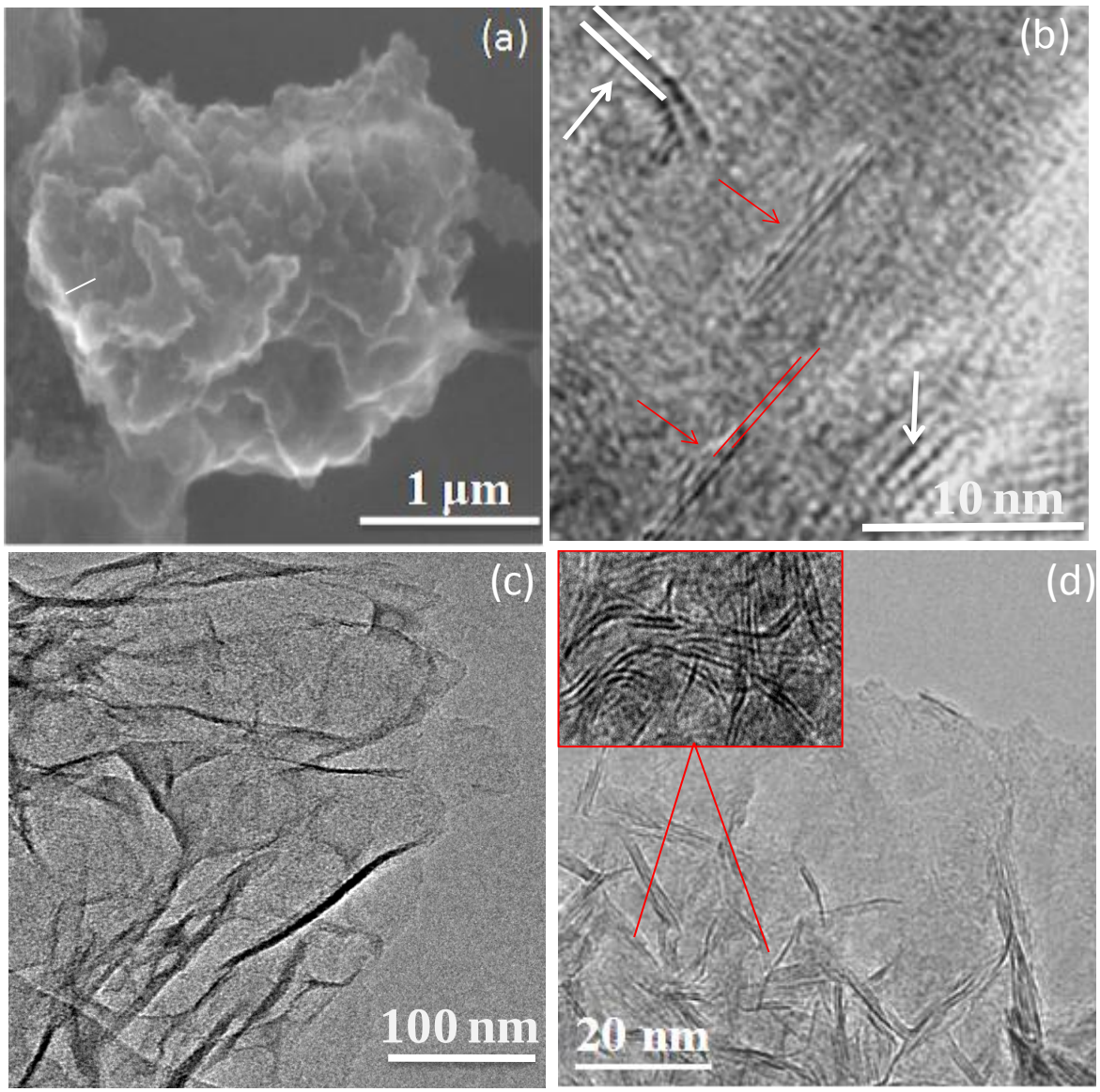

Fig. S11 (a) FESEM image of MoS_2 assemblies, (b) HRTEM image of MoS_2-RGO assemblies (white and red arrows indicate MoS_2 and RGO respectively), (c) TEM image of RGO and (d) HRTEM image of MoS_2/RGO physical mixture (Inset shows magnified portion).

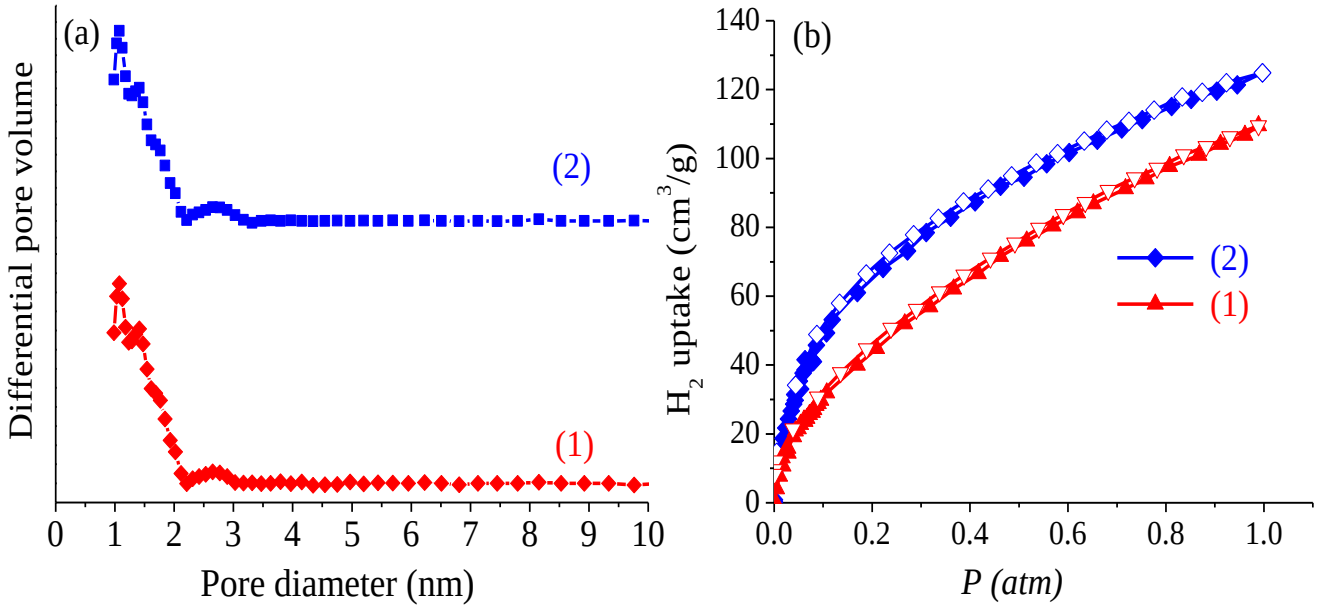

Fig. S12 (a) Pore size distribution curve, (b) Hydrogen sorption profile at 77 K of MoS_2 assemblies (1, red) and MoS_2-RGO assemblies (2, blue).

Serial. No	Composite	Activity (mmol h^{-1} g^{-1})	TOF (h^{-1})	References
1	**Few-layer MoS_2**	**0.07**	**0.01**	**Present Work**
2	**MoS_2 assemblies**	**1.75**	**0.84**	**Present Work**
3	**MoS_2-RGO (3:1)**	**1.38**	**0.98**	**Present Work**
4	**MoS_2-RGO (2:1)**	**1.30**	**0.94**	**Present Work**
5	**MoS_2-RGO (1:1)**	**0.35**	**0.40**	**Present Work**
6	MoS_2-RGO Composite	3	0.68	Ref (8)
7	MoS_2-EG Composite	0.54	0.21	Ref (8)

Table 1: Comparison of activity of catalyst in terms of yield of H_2 evolved.

(a) TOF calculated per mole of catalytically active material (Graphene considered as catalytically inactive)

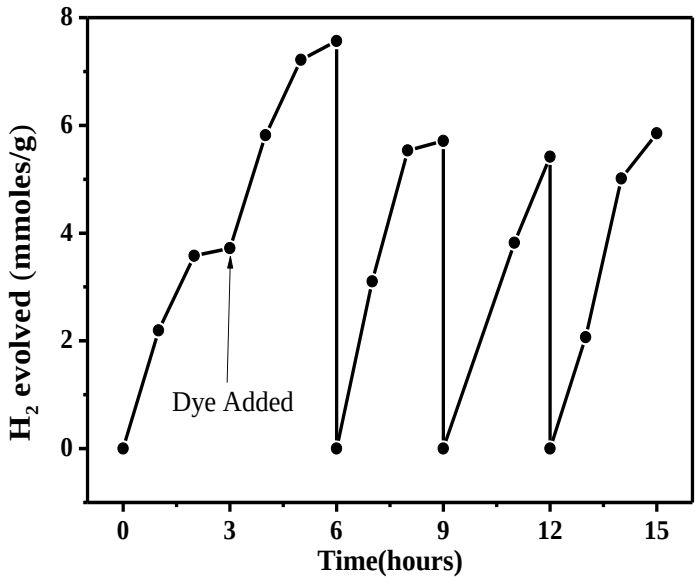

Fig. S13 Cycling studies of MoS_2 assemblies.

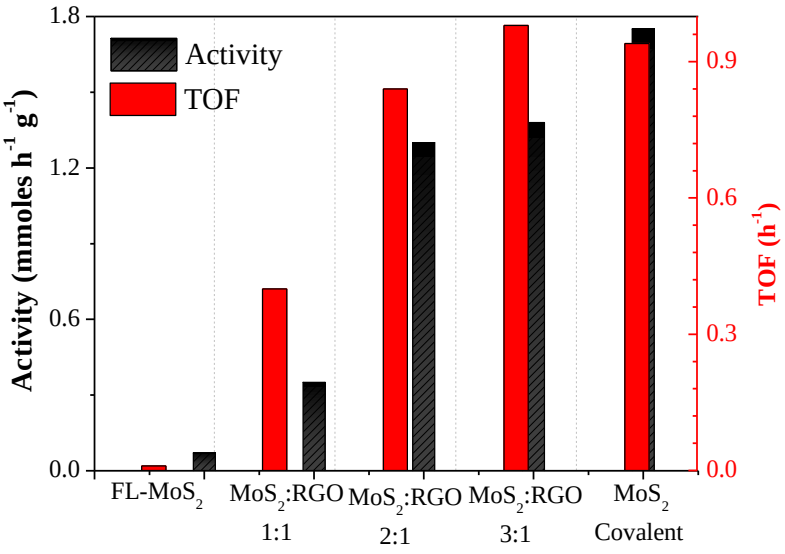

Fig. S14 Comparison of yield of H_2 (mmoles h^{-1} g^{-1}) evolved and TOF (h^{-1}) by MoS_2 assemblies and different ratio of MoS_2-RGO assemblies.

References:

1. Q. Li, A. V. Rukavishnikov, P. A. Petukhov, T. O. Zaikova, C. S. Jin, J. F. W. Keana, *J. Org. Chem.*, 2003, **68**, 4862; (b) A. Mangalum, R. J. Jr. Gilliard, J. M. Hanley, A. M. Parker, R. C. Smith, *Org. Biomol. Chem.*, 2010, **8**, 5620.