Electronic Supplementary Information

Molybdenum Sulfo-selenide Nanocomposites with Carbon Nanotube and Reduced Graphene Oxide for Photocatalytic Hydrogen Evolution Reaction

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1. Experimental

1.1 Chemicals used

Ammonium molybdate tetrahydrate, thiourea, and selenium powder are procured from SRL, SDFCL, and LOBA chemical limited respectively, while multi-walled carbon nanotube and graphene oxide are purchased from Reinste chemicals. All the chemicals and reagents are of analytical grade and used without any further purification.

1.2 Acid functionalization of multi-walled carbon nanotubes (MWCNTs)

To functionalize MWCNTs, 200 mg of pristine MWCNTs are dispersed in a 3:1 H_2SO_4/HNO_3 (10 ml) mixture and kept in refluxing condition at 100° C. under constant stirring for 12 h. [1] Then the mixture is allowed to rest for an hour where functionalized MWCNTs settle down at the bottom. Then the obtained MWCNTs are washed several times with water and ethanol by centrifugation, and dried in a vacuum oven at 60 °C.

1.3 Synthesis of MoSSe nanoflowers, MoSSe@CNT and MoSSe@RGO heterostructures

For the synthesis of MoSSe nanoflowers, ammonium molybdate tetrahydrate (molybdenum precursor, 1 mmol) and thiourea (7 mmol, sulfur precursor) are added to a water-ethanol-N-methyl pyrrolidone (25ml, 2:2:1 v/v) mixture in a beaker and kept under the

constant stirring condition to get homogeneous dispersion. In another beaker, selenium powder (3.5 mmol) is dispersed in hydrazine hydrate (10 ml) by sonication which forms black dispersion. Finally, both the solutions are mixed by stirring and then transferred to a 50 ml Teflon-lined stainless-steel autoclave, heated at 200^{o} C for 24 h in a furnace[2].

For the synthesis of MoSSe@CNT and MoSSe@RGO heterostructure, 30 mg of functionalized MWCNT and GO are added independently to the beaker containing molybdenum, sulfur, and selenium precursors and the above-mentioned procedure for bare MoSSe nanoflower synthesis is repeated.

1.4 Material Characterization

Field emission scanning electron microscope (FESEM) images are recorded using a JEOL, JSM-7100F, instrument at the operating voltage of 200 kV. Raman spectra are obtained using a Renishaw. UK using, a He-Ne laser with an excitation wavelength of 532 nm. Powder X-ray diffraction (PXRD) patterns are recorded using Rigaku Ultima IV with CuK_{α} radiation source. The photoluminescence (PL) spectra of an aqueous solution of eosin y with 10 ppm of nanocomposites are recorded using a PerkinElmer LS55 spectrofluorometer (excitation wavelength = 490 nm). X-ray photoelectron spectroscopy (XPS) PHI Versaprobe III is used to examine the-elemental composition and the oxidation state of the synthesized samples.

1.5 Photochemical studies

For photochemical HER, initially, eosin Y is dispersed in a water and triethanolamine mixture in a quartz vessel and then MoSSe@CNT and MoSSe@RGO nanocomposite is added, sonicated for 1 h. The quartz vessel is sealed with septa and illuminated with a 400 W xenon lamp. The evolved H_2 gas is collected from the headspace of the vessel and analyzed through a gas chromatogram (PerkinElmer, ARNL 580C) equipped with a thermal conductivity detector.

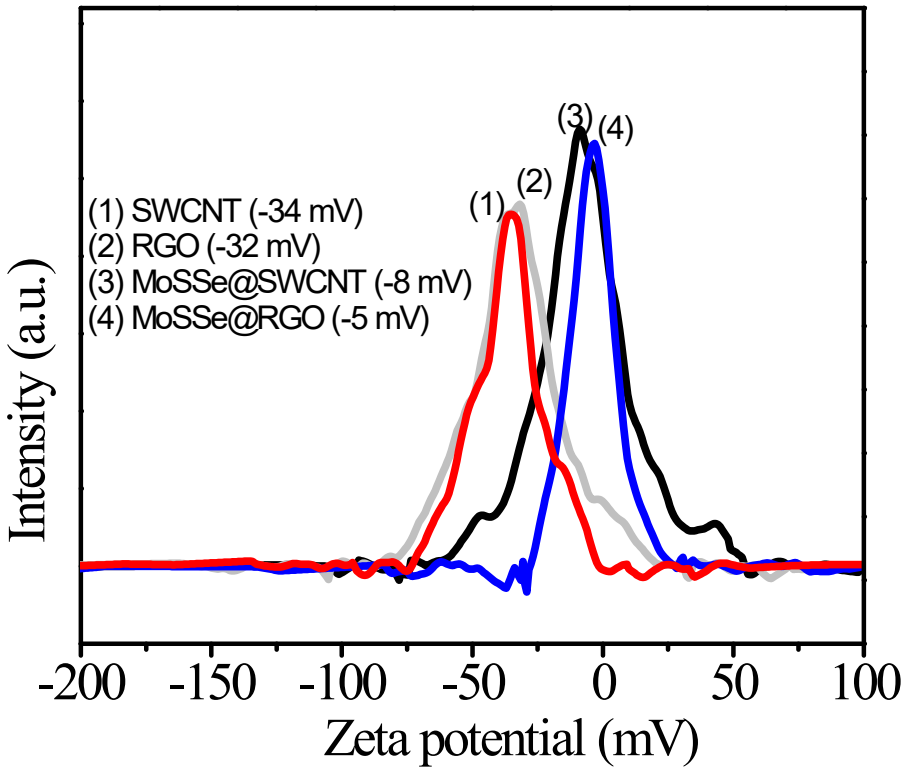

Figure S1. Zeta potential plots for functionalized SWCNT (1), RGO (2), MoSSe@SWCNT (3) and MoSSe@RGO (4).

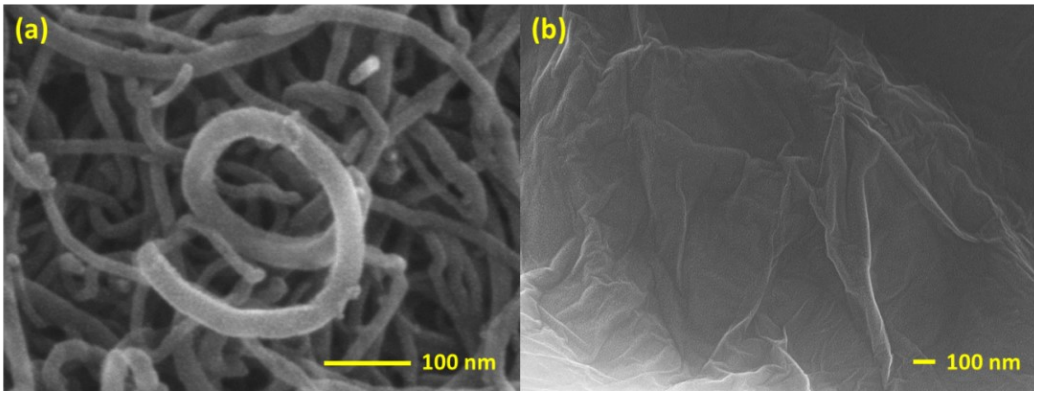

Figure. S2 FESEM images of (a) carboxyl-functionalized MWCNT and (b) graphene oxide.

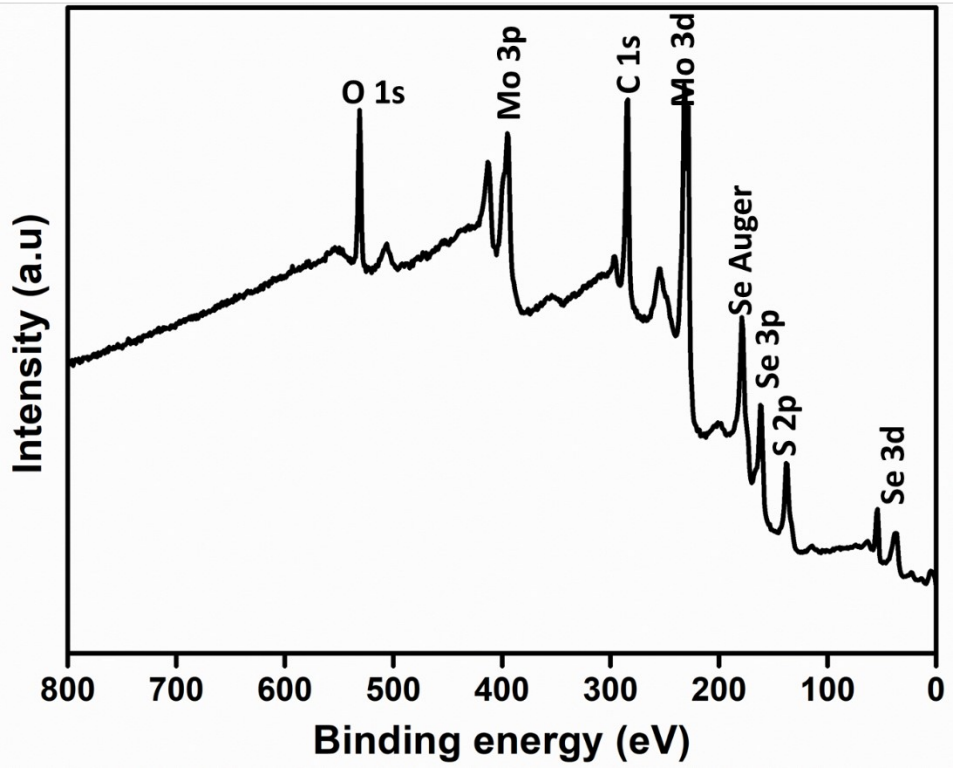

Figure. S3 X-ray photoelectron survey spectra of MoSSe/RGO nanocomposites.

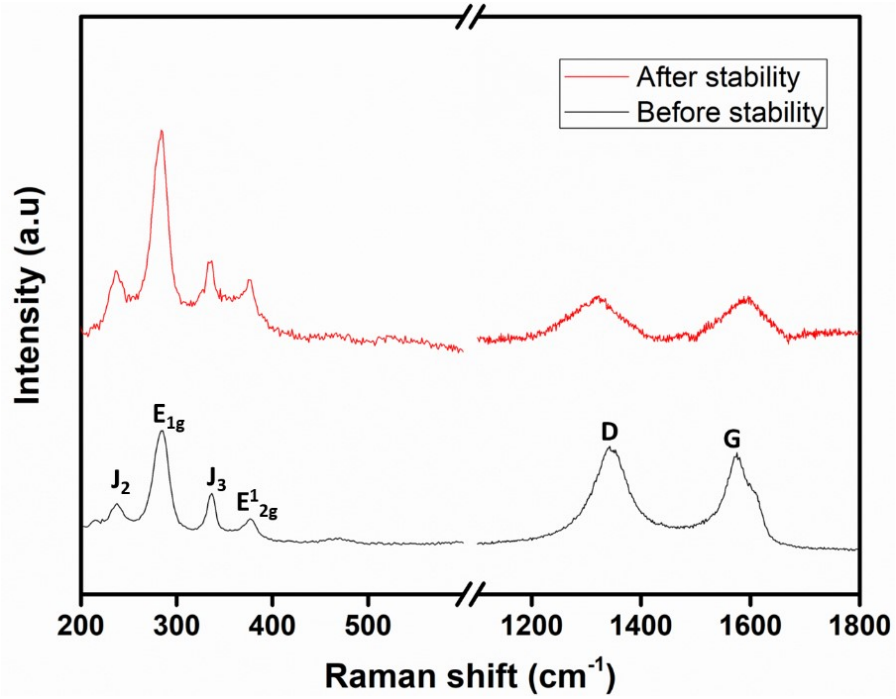

Figure. S4 Raman spectra of MoSSe/RGO nanocomposite before and after cycle stability test.

Table. S1 *Comparison of the photocatalytic HER performance of MoSSe@CNT and MoSSe@RGO nanocomposites with TMDCs-based nanocomposites including graphene, graphitic carbon nitride (g-C_3N_4) and black phosphorous.*

Photocatalyst	**Reaction condition (Light source, Sacrificial agent)**	**Activity (μmol h^{-1} g^{-1})**	**Reference**
EY/MoS2-P.BCN	400 W xenon lamp, TEOA	4064	[3]
EY/P.RGO/MoS_2	400 W xenon lamp TEOA	3682	[4]
EY/ MoSeTe	400 W xenon lamp, TEOA	3200	[5]
MoS_2/Black phosphorous	300 W xenon lamp, Na_2S/Na_2SO_3	1286	[6]
g-CN/NSGQDs	400 W xenon lamp, TEOS	4340	[7]
EY/MoS2-P.SWCNT	400 W xenon lamp, TEOA	4939	[3]
* MoS_2 nanosheets/g-C_3N_4 nanosheets	300 W xenon lamp TEOA	1155	[8]
WSSe	300 W xenon lamp Na_2S/Na_2SO_3	3647	[9]
EY/$MoTe_2$	400 W xenon lamp, TEOA	1100	[5]
EY:/MoS_2/g-C_3N_4	400 W xenon lamp, TEOA: H2O	1157	[10]
EY/MoSSe	**400 W xenon lamp TEOA**	**1754**	**Present work**
EY/MoSSe@CNT		**3622**	
EY/MoSSe@RGO		**5016**	

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