

## Supporting Information:

# Facile and one-step synthesis of free standing 3-D MoS<sub>2</sub>/Mo and MoS<sub>2</sub>-rGO/Mo binder free electrode for efficient hydrogen evolution reaction

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## Experimental Section:

Materials: Molybdenum foil (0.127mm, 99.99% trace metal basis) was purchased from Sigma Aldrich. Thiourea and 30% H<sub>2</sub>O<sub>2</sub> were acquired from SDFCL. Millipore water obtained from a Milli-Q system was used throughout the experiment.

The molybdenum foil was cut into 5 cm x 1cm pieces. The as obtained pieces were cleaned with 2M HCl, followed by ultrasonication in 3:1 v/v H<sub>2</sub>O: Acetone solution for 20 minutes. The foil was then washed with copious amount of water and air-dried.

1.5 g thiourea was dissolved in 30mL water by stirring for 10 minutes, the solution was then placed in a Teflon-lined autoclave of 50 mL capacity in which the Mo foil was placed in an inclined position.

The autoclave was then heated to 180 °C at a ramping of 6 °C/min and maintained for 18 h. The autoclave was then allowed to cool to room-temperature naturally. The foil was removed using a Teflon-tape coated forceps and was sequentially with copious amount of water and ethanol and air-dried under ambient condition.

The MoS<sub>2</sub>-rGO/Mo hybrids was similar experimental technique only added the GO solution in the reaction mixture. After the reaction, the GO gets reduced hydrothermally to formed rGO on the Mo substrate and MoS<sub>2</sub> grown on the rGO layer. Finally it's formed MoS<sub>2</sub>-rGO/Mo 3-D electrode.

## Physical characterizations:

The Raman measurement was performed on a Raman system (WITec) with confocal microscopy at room temperature using a Nd:YAG laser (532 nm) as an excitation source. Field emission Scanning electron microscope (FE-SEM) images and Energy-dispersive X-ray spectroscopy (EDS) spectra was acquired on a FE-SEM, FEI-INSPECTF50 instrument by FEI technology. Transmission electron microscope (TEM), high resolution TEM (HRTEM) images and selected area electron diffraction (SAED) patterns were obtained with a TEM, JEOL-JEM-2100F operated a 200kV accelerating voltage. The TEM sample was prepared by carefully scratching off a portion from the Mo foil which was then dispersed in ethanol by ultrasonication. 2 μL of the solution was drop-casted on carbon coated copper grid (300mesh), and then dried for TEM analysis. X-ray photoelectron spectroscopy (XPS) was performed for the elemental analysis which were carried out on an ESCALAB 250

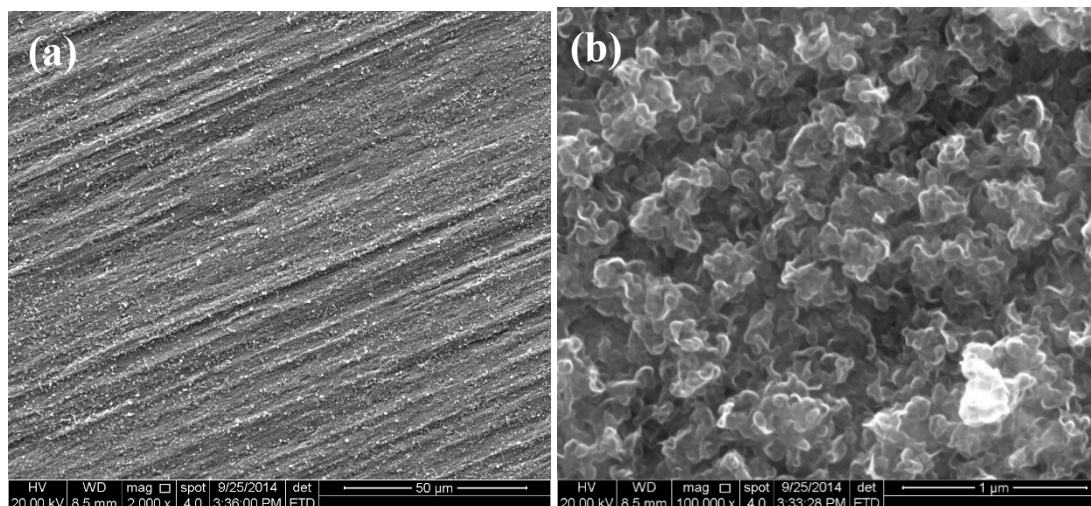
(Thermo Electron) with a monochromatic Al  $K_{\alpha}$  (1486.6 eV) source. The surface atomic concentrations were determined from photoelectron peaks areas using the atomic sensitivity factors reported by Scofield. The binding energy was calibrated by placing the principal C1s peak at 284.6 eV.

### Electrochemical measurements:

All the electrochemical analysis was performed using an electrochemical workstation (CHI760E CH Instrument, USA) with a typical three electrode system. Platinum coil was used as the counter electrode, Ag/AgCl (3M KCl) as the reference electrode and the MoS<sub>2</sub>@Mo foil was directly used the working electrode. The electrolyte used was 1M H<sub>2</sub>SO<sub>4</sub> saturated with N<sub>2</sub> gas flow for 30 minutes to remove the dissolved oxygen. During the measurement, flow of N<sub>2</sub> was maintained on the headspace of electrolyte to minimize the disturbance due to gas purging. The Linear Sweep Voltametry (LSV) measurements were at a scan rate of 5mV/s. For testing the stability of the catalyst Chronoamperometry (CA) was performed at an overpotential of ( $\eta$ ) of 210 mV. All the measurements were done at room temperature. All the potential values were measured against Ag/AgCl (3M KCl) electrode which was then converted to RHE according to the following equation:

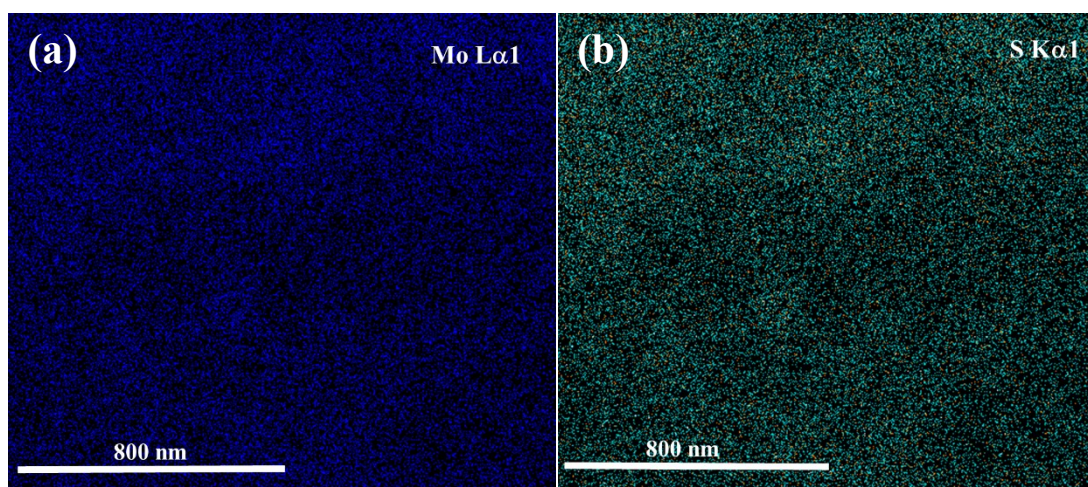
$$E_{\text{RHE}}(\text{V}) = E_{\text{Ag/AgCl}} + 0.235 \text{ V (at } 25^{\circ}\text{C in the acidic solution having pH=0)}$$

### ESI-1



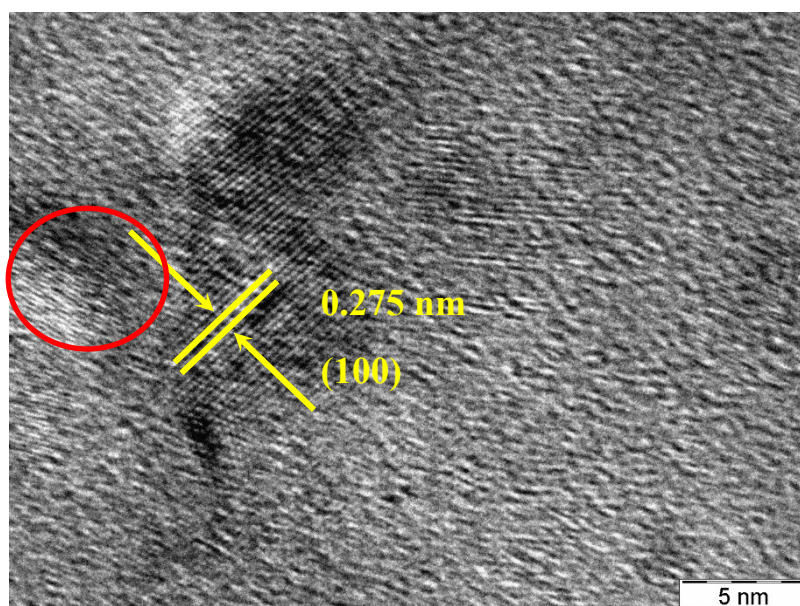
**Fig.1** (a and b) Low and high magnified SEM image of uniformly and large area synthesis of MoS<sub>2</sub> on Mo foil.

## ESI-2



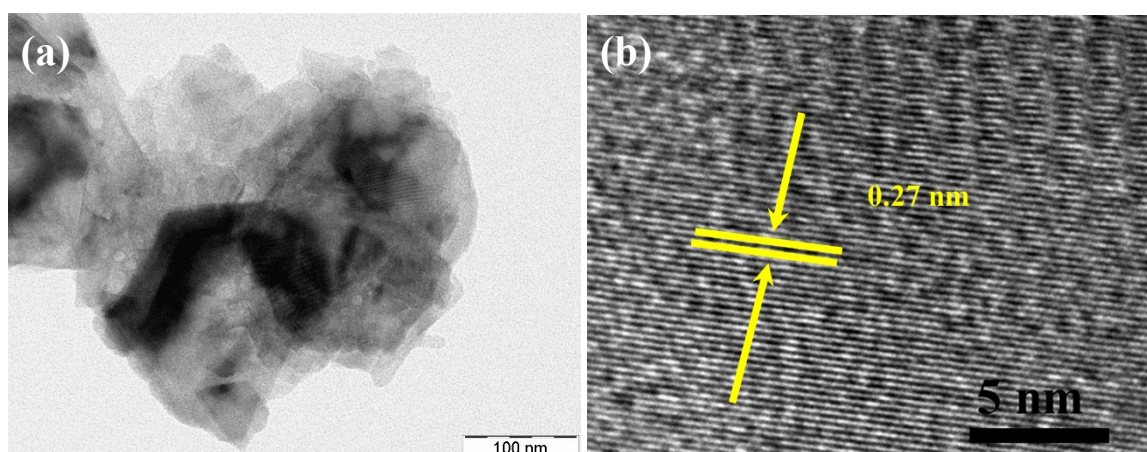
**Fig.2** (a and b) elemental mapping of Mo L $\alpha$ 1 and S K $\alpha$ 1 of MoS<sub>2</sub>/Mo hybrids synthesis by hydrothermally.

## ESI-3



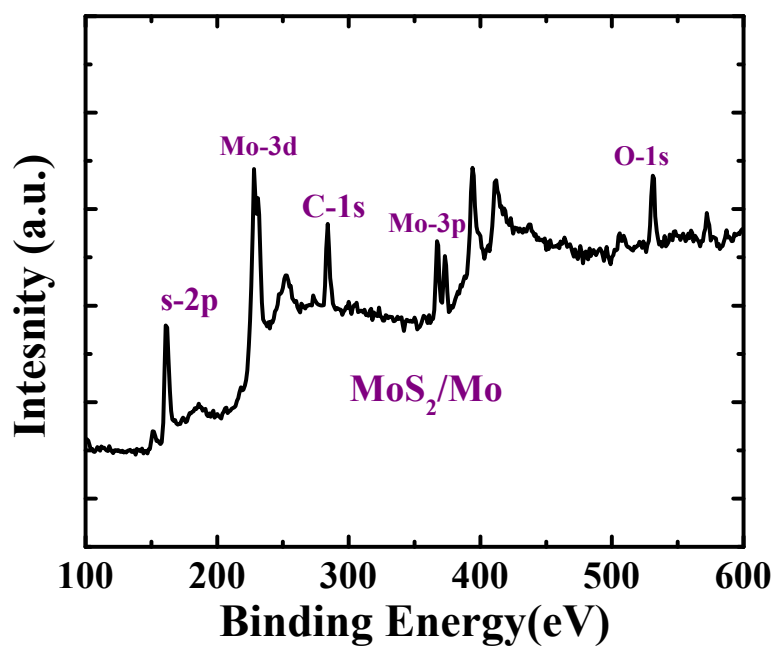
**Fig.3** Display the HRTEM image of MoS<sub>2</sub> grown on the Mo substrate.

#### ESI-4



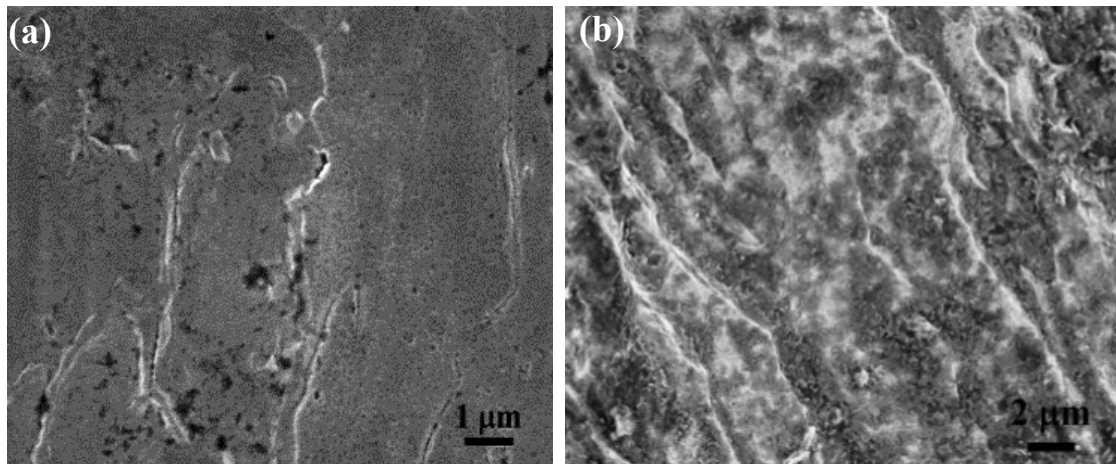
**Fig.4** (a and b) TEM and HRTM images of commercial MoS<sub>2</sub> nanostructure.

#### ESI-5



**Fig.5** XPS survey spectra of MoS<sub>2</sub>/Mo hybrid structure.

## ESI-6



**Fig.6** Surface morphology of virgin (a) Mo foil and (b) that recovered after the first cycle.

## ESI-7: Calculation of etching rate from 3-D MoS<sub>2</sub>/Mo hybrid by H<sub>2</sub>O<sub>2</sub>:

In order to estimate the etching rate ( $t$ ) for each cycle, we measured the weight ( $w_1$ ) before the Mo foil before and after the growth as well as the weight ( $w_2$ ) after the etching. If the area is known, the etching thickness can easily be obtained using the following equation,

$A\rho t = w_1 - w_2$  where  $\rho$  is the density of Mo and  $A$  is the area.

Area  $A$  of the foil = 4.6 cm<sup>2</sup>

Density  $\rho$  of Mo foil = 10.2 g/cm<sup>3</sup>

Initial weight ( $w_1$ ) of Mo foil: 0.4828 g

Weight of MoS<sub>2</sub>/Mo hybrid: 0.4958 g

Weight ( $w_2$ ) after treatment with the H<sub>2</sub>O<sub>2</sub>: 0.4177 g

Based on the above equation, the etching rate is estimated as

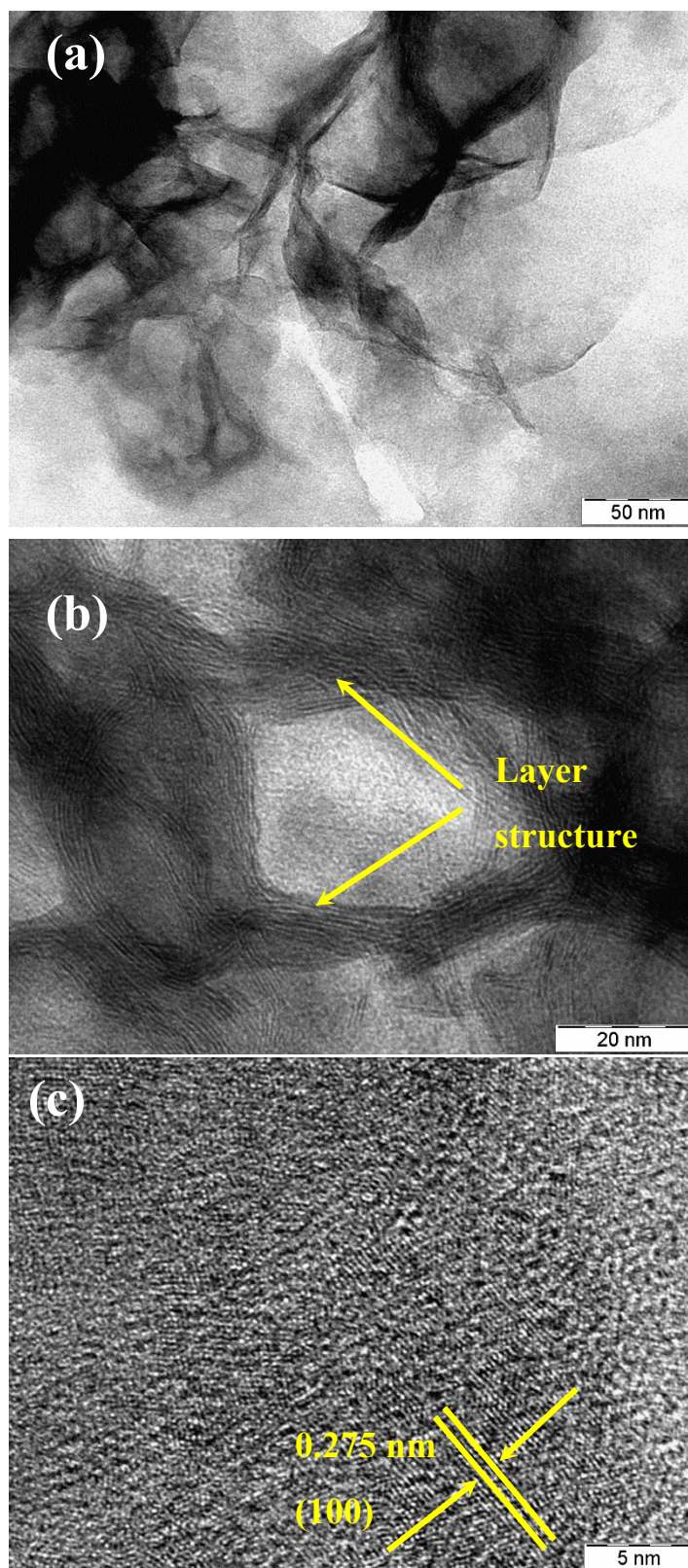
$$t = (0.4815 - 0.4177) / (4.6 * 10.2) = 13.6 \mu\text{m}$$

As the foil was etched from the both side, the etching of the etch side of the foil

$$= 13.6 / 2 \mu\text{m}$$

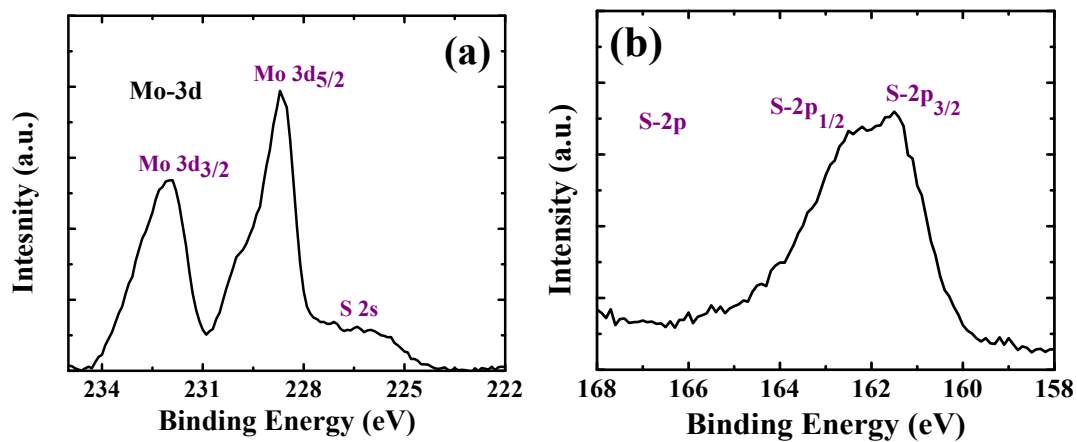
$$= 6.8 \mu\text{m per cycle}$$

Similarly, the deposition of MoS<sub>2</sub> is found to be 1.4 mg/cm<sup>2</sup>.



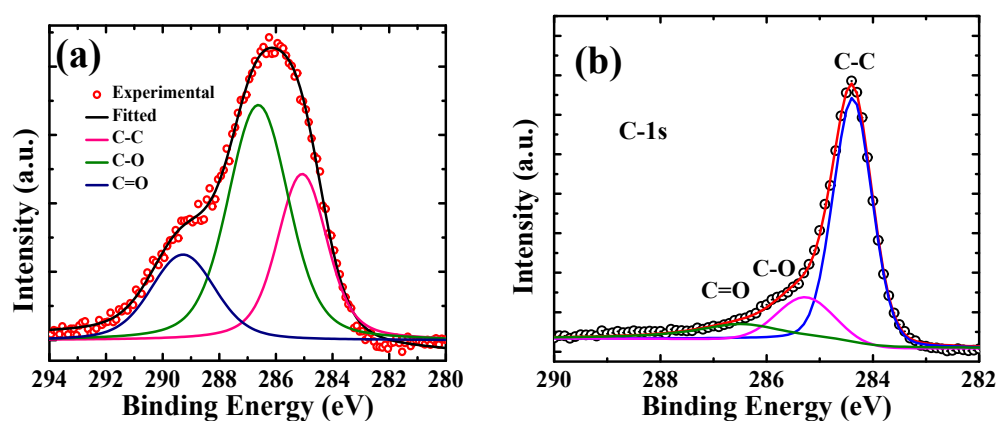
**Fig.7** (a and b) Low and high magnified TEM images of MoS<sub>2</sub>-rGO/Mo hybrids. (c) HRTEM images of MoS<sub>2</sub>-rGO/Mo hybrids.

## ESI-9



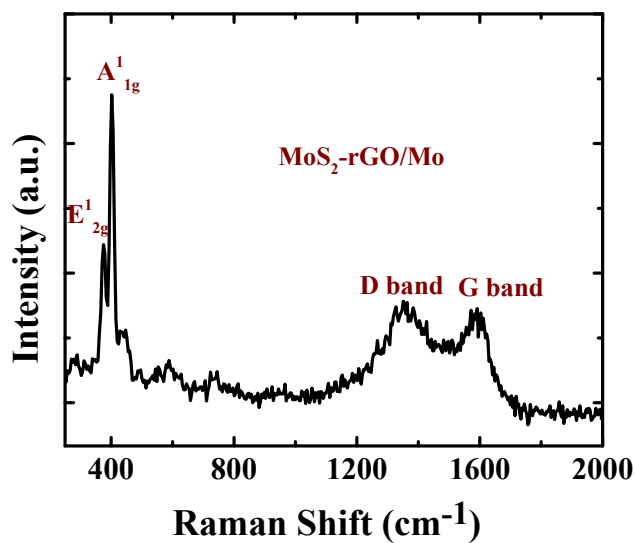
**Fig.8 (a and b)** high resolution XPS spectra of Mo 3d and S 2p of MoS<sub>2</sub>-rGO/Mo hybrid nanostructures.

## ESI-10



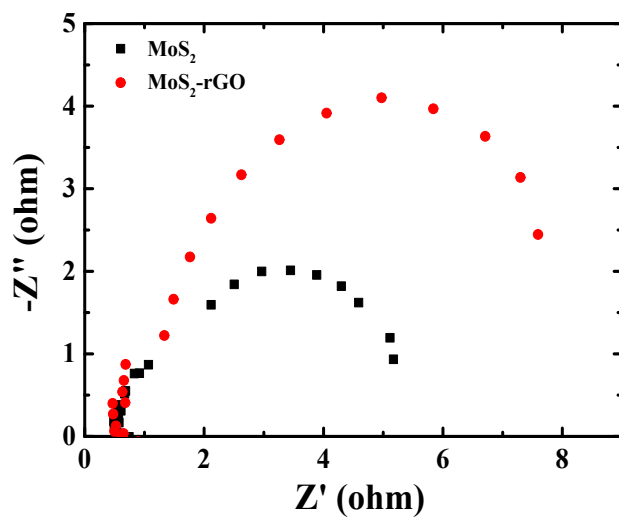
**Fig.9 (a and b)** De-convoluted C-1s spectra of GO and rGO in MoS<sub>2</sub>-rGO/Mo hybrid, respectively.

### ESI-11



**Fig.10** Raman spectrum of MoS<sub>2</sub>-rGO/Mo hybrid nanostructures. It reveals the signature of both the MoS<sub>2</sub> and rGO.

### ESI-12



**Fig.11** Electrochemical impedance spectra of MoS<sub>2</sub>/Mo and MoS<sub>2</sub>-rGO/Mo hybrid electrode in 1 M H<sub>2</sub>SO<sub>4</sub> solution.



**Table-S1: Comparison of HER activity of current state of art Molybdenum chalcogenide,**

Catalyst	Electrolyte	$\eta$ (mV)		Tafel slope (mV/dec)	$C_{dl}$ ( $\mu\text{F}/\text{cm}^2$ )	Reference
		10 mA/cm <sup>2</sup>	100 mA/cm <sup>2</sup>			
MoS <sub>2</sub> /Mo foil	0.5 M H <sub>2</sub> SO <sub>4</sub>	>300 mV (@ 1 mA/cm <sup>2</sup> )		75	-	1
MoSe <sub>2</sub> /Mo foil	0.5 M H <sub>2</sub> SO <sub>4</sub>	>300 mV (@ 1 mA/cm <sup>2</sup> )		68	-	1
Electrochemically tuned VA MoS <sub>2</sub> films	0.5 M H <sub>2</sub> SO <sub>4</sub>	~ 210	-	43-47	-	2
Defect rich MoS <sub>2</sub> nanosheets	0.5 M H <sub>2</sub> SO <sub>4</sub>	~ 150	-	50	-	3
Core-shell MoO <sub>3</sub> -MoS <sub>2</sub> nanowires	1M H <sub>2</sub> SO <sub>4</sub>	~ 255	-	50 - 60	-	4
Monolayer MoS <sub>2</sub> film	0.5 M H <sub>2</sub> SO <sub>4</sub>	~ 420 @ 1mA/cm <sup>2</sup>	-	140-145	66.7	5
Cubane- type [Mo <sub>3</sub> S <sub>4</sub> ] <sup>4+</sup>	0.5 M H <sub>2</sub> SO <sub>4</sub>	~ 230	-	120	-	6

N-doped 1T-2H MoSe <sub>2</sub> /Graphene shell-core nanoflakes array	0.5 M H <sub>2</sub> SO <sub>4</sub>	98	–	49	136	7
O-MoS <sub>2</sub> /rGO	0.5 M H <sub>2</sub> SO <sub>4</sub>	170	–	40	598	8
Au-MoS <sub>2</sub> (808)	0.5 M H <sub>2</sub> SO <sub>4</sub>	~235	–	71	–	9
Edge oriented nanoporous MoS <sub>2</sub> film	0.5 M H <sub>2</sub> SO <sub>4</sub>	~250	–	50	12.5	10
CLET-MoS <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	~ 180	–	39	–	11
O <sub>2</sub> plasma treated monolayer MoS <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	> 600	–	171	–	12
1T MoS <sub>2</sub> nanosheets	0.5 M H <sub>2</sub> SO <sub>4</sub>	~ 200	–	40	–	13
Double-gyroid MoS <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	> 250	–	50	4.8 x 10 <sup>3</sup>	14
Petaled MoS <sub>2</sub> -Mo	0.5 M H <sub>2</sub> SO <sub>4</sub>	242	–	68	1.7 x 10 <sup>4</sup>	15
MoS <sub>2</sub> /Mo foil	1 M H <sub>2</sub> SO <sub>4</sub>	188	334	64	7.2 x 10 <sup>4</sup>	<b>This work</b>

MoS <sub>2</sub> -rGo@Mo foil	1 M H <sub>2</sub> SO <sub>4</sub>	172	294	52	9 x 10 <sup>4</sup>	<b>This work</b>
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