Electrochemical measurements: Electrochemical measurements were carried out with a three electrode system on a Metrohm autolab electrochemical workstation (Zahner, Germany). Briefly, a glassy carbon (GC) electrode with a diameter of 3 mm served as a substrate for the working electrode. Platinum disk electrode and Ag/AgCl (3.5 M KCl) were used as counter and reference electrodes, respectively. To prepare the working electrode, 10 mg of the catalysts were dispersed in the water- ethanol mixture (1:4) and 50 μL of 5 wt% Nafion solutions, and further ultrasonicated to form a uniform black ink. Next, 10 μL of catalyst ink was pipette onto the glassy carbon surface to result in a 1.3 mg cm^{-2} loading for all samples including commercial Pt/C catalyst (20 wt%, Johnson Matthey). Further, N_2 flow was used through the electrolyte in the cell for 30 min to saturate it. The Linear Sweep voltammetry (CV) experiments were performed in N_2-saturated 0.5 M aqueous H_2SO_4 electrolyte solutions with a scan rate of 10 mV s^{-1}. All potentials reported were referenced to the reversible hydrogen electrode (RHE) through a RHE calibration. Equation 1 was used for the conversion of potential from Ag/AgCl to RHE.

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + E_{Ag/AgCl}^{0} \quad (1)$$

$$(E_{Ag/AgCl}^{0} = +0.199V)$$

The overpotential (η) was calculated at different current density (x) using Equation (2) as

$$\eta^{x} = E_{RHE} - 1.23 \quad (2)$$

Turnover frequency (TOF) was calculated using equation -

$$TOF = jS/4Fn \quad (3)$$

where S defines the area (cm^2) of electrode with active materials, j represents the measured current density (A cm^{-2}) at desired η, F is the Faraday constant, the parameter 4 in denominator corresponds to number of electrons involved in OER reaction, and n represents the number of moles of the catalytic material on the working electrode. TOF was calculated with respect to metals as obtained by SEM-EDS analysis. Number of moles of metals per unit surface area can be obtained according to Equation 4, as

$$n^{Ni} = \text{catalyst loading} \times \% \text{ weight of Ni/Atomic weight of Ni} \quad (4)$$

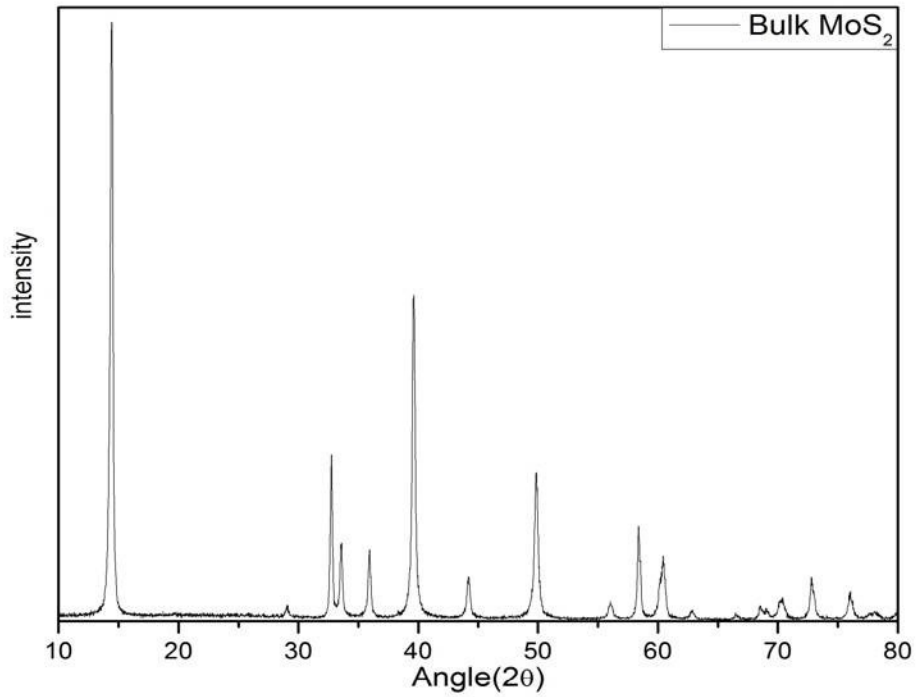

Figure S1: XRD of bulk MoS_2.

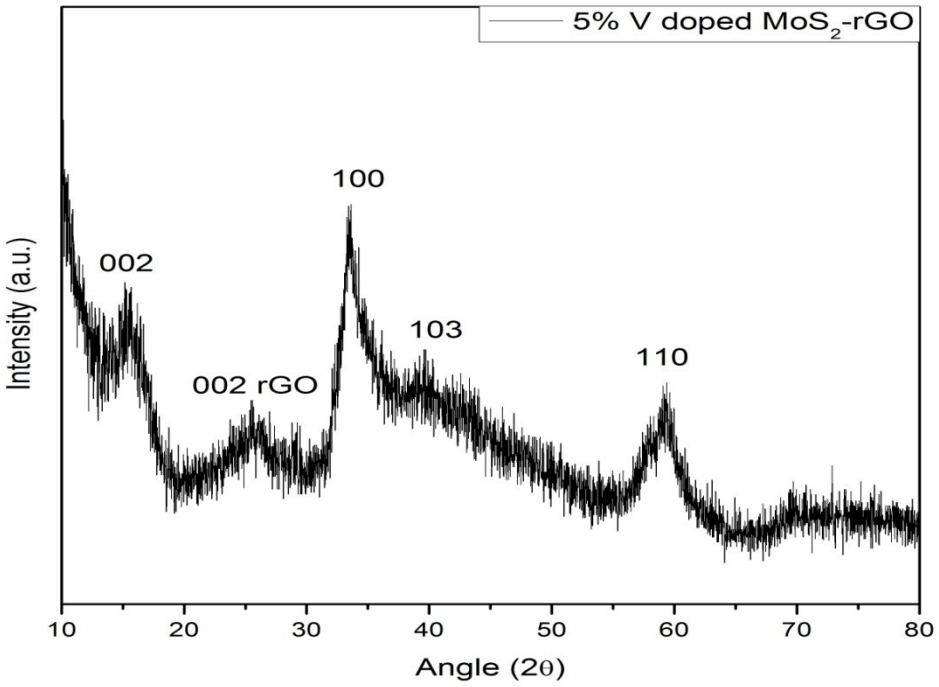

Figure S2: XRD of 5% V doped MoS_2-rGO.

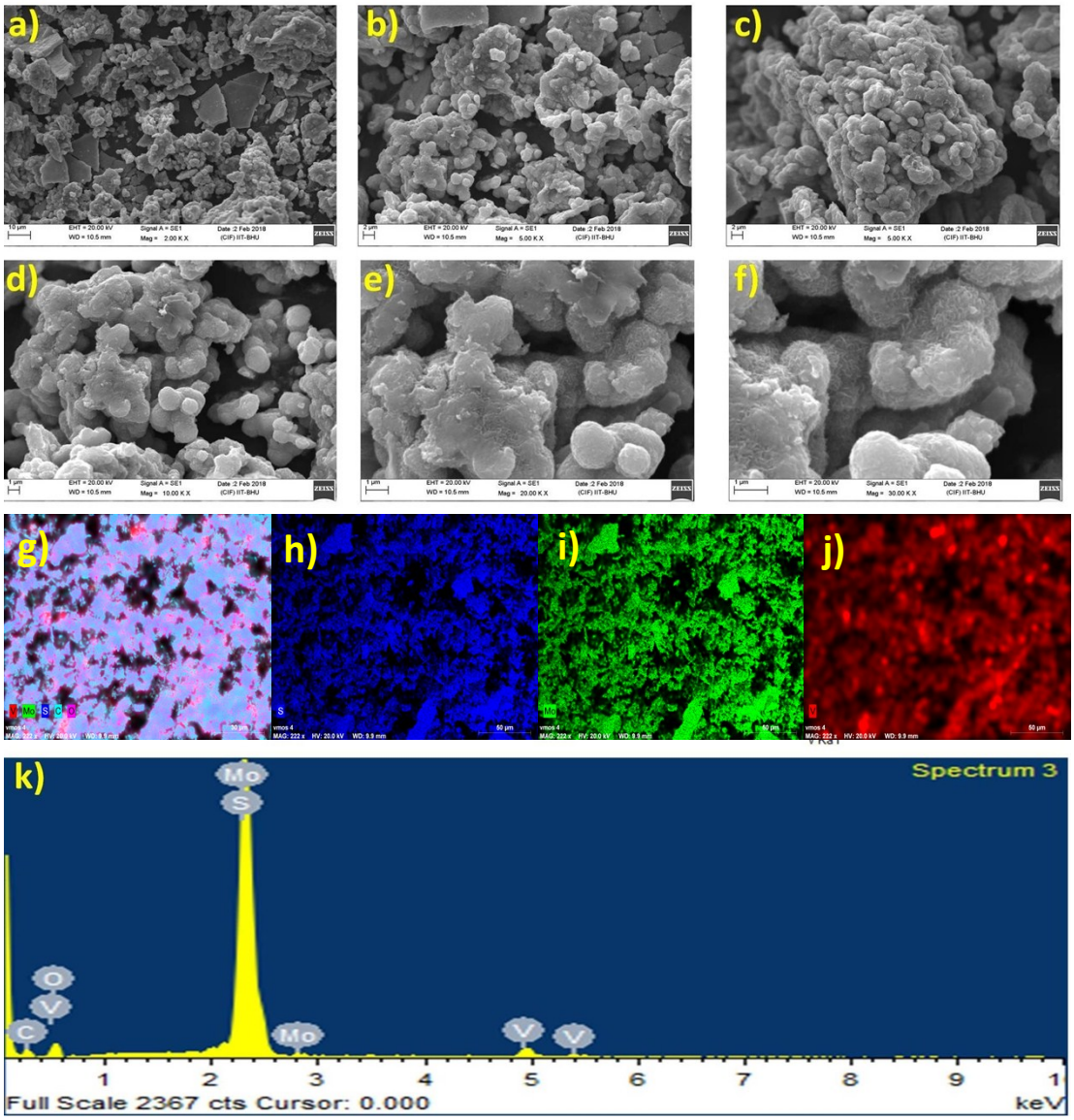

Figure S3: (a-f) SEM images, (g) collective element mapping, (h) S mapping, (i) Mo mapping, (j) V mapping, and (k) EDX spectrum of 5% V-doped MoS_2-rGO

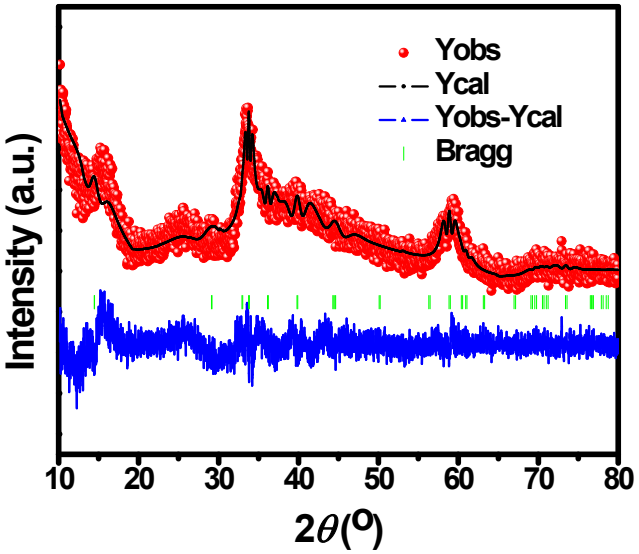

Figure S4: Le-bail profile fitting of MoS_2-rGO.

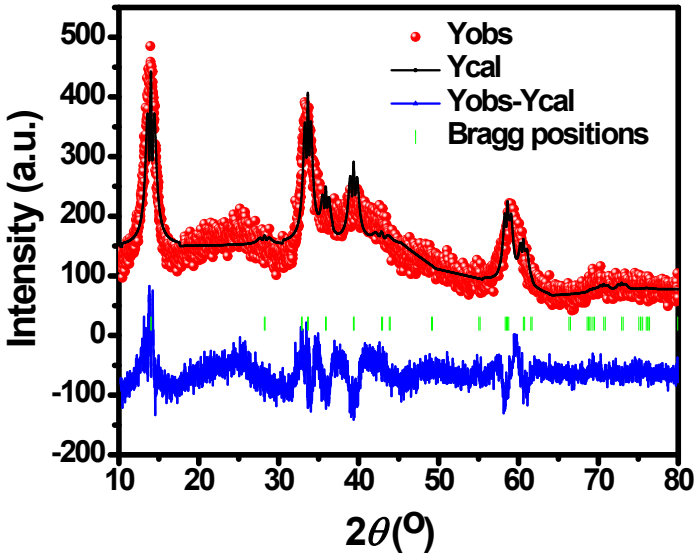

Figure S5: Le-bail profile fitting of 5% MoS_2-rGO.

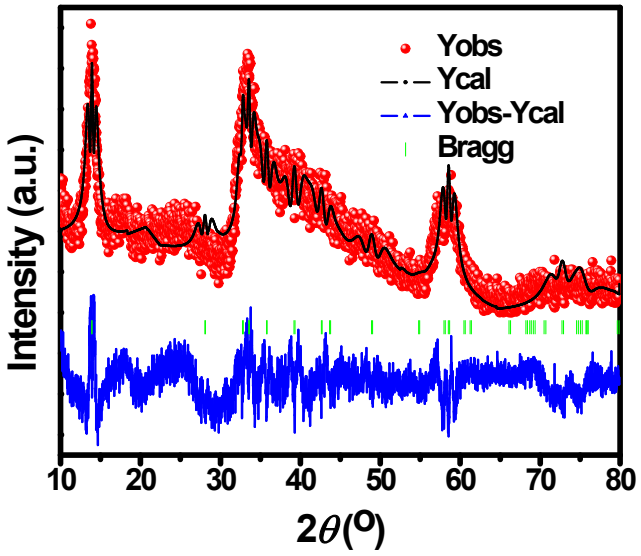

Figure S6: Le-bail profile fitting of 10% MoS_2-rGO.

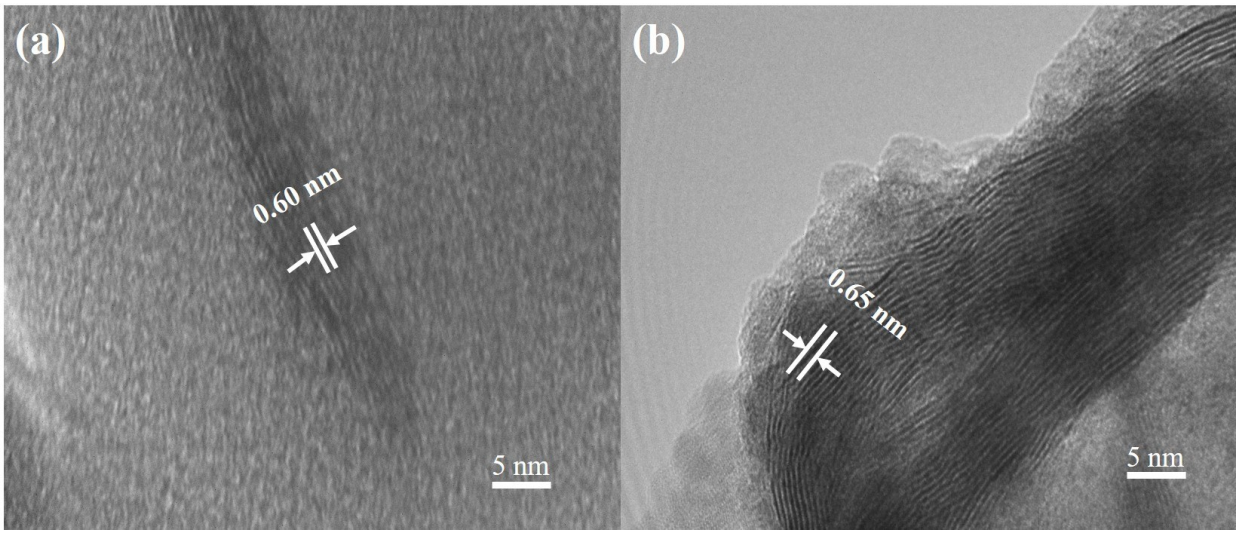

Figure S7: HRTEM of (a) undoped and (b) 10% V doped MoS_2-rGO.

Table S1: Le-bail refinement parameters for MoS_2-rGO, 5% and 10% V doped MoS_2-rGO.

	MoS_2-rGO	**5% V doped MoS_2-rGO**	**10% V doped MoS_2-rGO**
a, b	3.137139	3.1460	3.151664
c	12.255086	12.6447	12.719102
Alpha, beta	90.0	90.0	90.0
gamma	120.0	120.0	120.0
Vol	104.451(0.170)	108.383	109.413(4.058)
RF-factor	1.58	1.39	1.58
Bragg R-factor:	0.418	0.906	2.48
Rp	35.7	68.7	31.7
Rwp	38.8	48.9	0.148E+04
Re	29.1	30.1	17.3
Chi^2	1.773	2.645	7288.

TableS2: Comparative study of various catalysts for HER

Electrocatalysts	Over potential(mV)	Tafel slope (mv/decade)	Electrolyte	Reference
Ni	370	118	1M NaOH	51
Pt	570	130	8M KOH	52
Ni-CNT	180	N/A	1M KOH	53
MoS_2 NSs	250	82	0.5 M H_2SO_4	54
MoS_2/CNT	199	61	0.5 M H_2SO_4	54
MoS_2 dots on Au	201	82	0.5 M H_2SO_4	55
MoS_2 dots /nanosheet hybrid on Au		74	0.5 M H_2SO_4	55
Graphene coated Cu NW	252	63	0.5 M H_2SO_4	56
MoS_2NFs/rGO		95	0.5 M H_2SO_4	57
MoS_2AGs/rGO		102	0.5 M H_2SO_4	57
V-doped MoS2/rGO composite	153	71	0.5M H_2SO_4	Our work