

Supporting Information

Doping of MoS₂ by ‘Cu’ and ‘V’: An Efficient Strategy for the Enhancement of Hydrogen Evolution Activity

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Preparation of working electrode: To prepare the ink of MoS₂-NS, MoS₂-TS, and M-MoS₂-TS (M = Cu, V, Zn, Mn, Fe, Sn) 5 mg synthesized catalyst was dispersed in 30 μ L of nafion and 300 μ L of isopropanol. Here isopropanol used as a dispersing solvent and nafion function as the binder. Then for uniform dispersion, whole dispersion was sonicated for 30 min. 3 μ L dispersion was drop casted carefully on GC electrode having diameter 3 mm which leads catalyst loading 0.63 mg/cm².

Electrochemical measurement:

Hydrogen evolution reaction were carried out in a three-electrode system. In this case calomel electrode used as a reference electrode, catalyst drop casted glassy carbon electrode as the working electrode, and graphite electrode used as a counter electrode. 10 mL of 0.5 M H₂SO₄ was used as an electrolyte. All the electrochemical data was recorded in CH Instrument (CHI604E) at 25 °C. The linear-sweep voltammogram of MoS₂-NS, MoS₂-TS, all M-MoS₂-TS were obtained from the potential range of 0.0 V to -0.85 V vs. calomel in 0.5 M H₂SO₄ with a scan rate of 5 mV/S.

Electrochemical Impedance Spectroscopy:

Electrochemical impedance measurement was also performed in a three-electrode system. Onset potentials of different materials were chosen as the performing bias for this measurement with the sweeping of frequency from 50 KHz to 1 Hz.

Characterization of Materials:

Shimadzu Spectrophotometer (model no. UV-2450) with a deuterium and tungsten-halogen lamp was used to study ultra-violet visible spectroscopy. Rigaku Mini Flex II diffractometer with Cu K α radiation was utilized to monitor the powder X-ray diffraction pattern, with a scanning rate of 2° per min and 0.5° per min. Microscope version, XT Platform version, XT UI version, Modal- "APREO S" FE-SEM was used to investigate the morphology of the synthesized MoS₂-NS, MoS₂-TS, all M-MoS₂-TS. EDS Analysis was carried out for these samples using the EDS attachment with FESEM which is Aztec (software), X-MaxN, NS: 77887 (Detector) of Oxford company. Raman analysis was carried out using HORIBASCI Raman instrument (model no LabRAM HR EVO). The detector is thermoelectrically cooled charged coupled device (CCD) detector of 576×384 pixels. Raman analysis is carried out upon excitation with 532 nm laser power. Using transmission electron microscopy (operated

with a Bruker microscope) morphology and crystallinity was determined of as synthesized catalysts. XPS (X-ray photoelectron spectroscopy) computation was carried out by Omicron EA 125 source using Al K α radiation having energy 1486.7 eV. During the course of measurement, base pressure was maintained $< 10^{-9}$ mbar in the UHV. AFM analysis was carried out using Bruker nanoscope multimode 8 AFM.

Calculation Method:

Details for the calculations of mass activity is given below. The mass activity value (A/g) was calculated from the catalyst loading and the observed current density (mA/cm_{geo}²) at a potential of -0.4 V vs. RHE.

Mass activity = observed current density at a fixed potential / catalyst loading

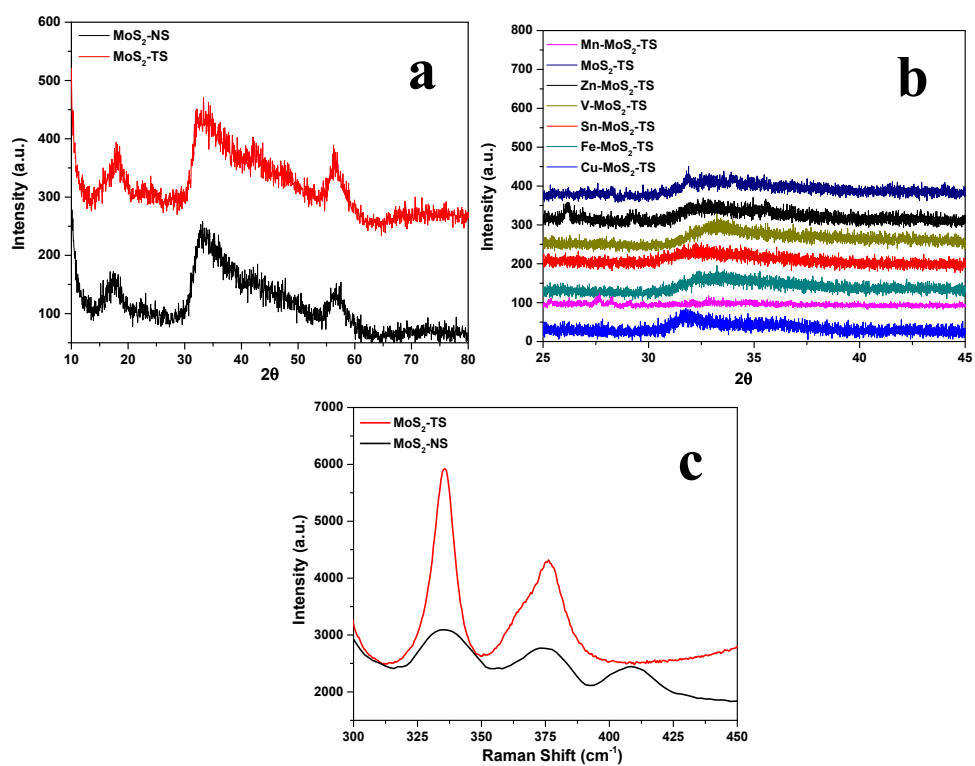


Figure S1: Comparative XRD pattern of (a) $\text{MoS}_2\text{-NS}$ and $\text{MoS}_2\text{-TS}$, (b) all $\text{M-MoS}_2\text{-TS}$ (scan range 2θ of $25\text{-}45^\circ$), (c) Raman spectra of $\text{MoS}_2\text{-NS}$ and $\text{MoS}_2\text{-TS}$.

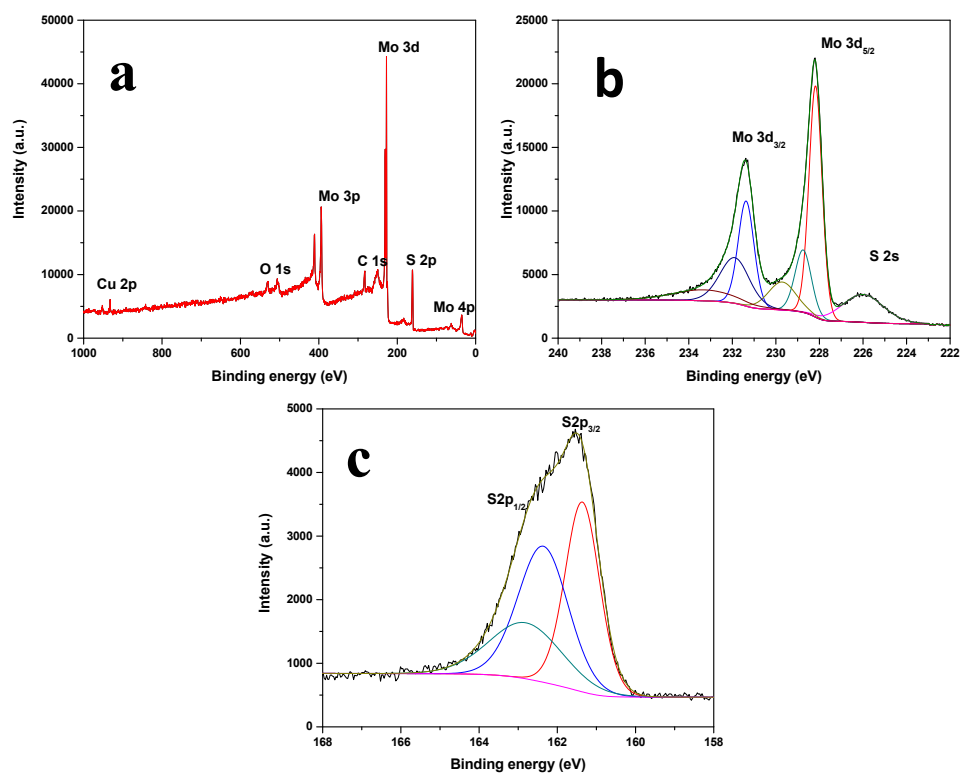


Figure S2: XPS spectra of Cu-MoS₂-TS, (a) survey spectra, (b) Mo 3d (c) S 2p.

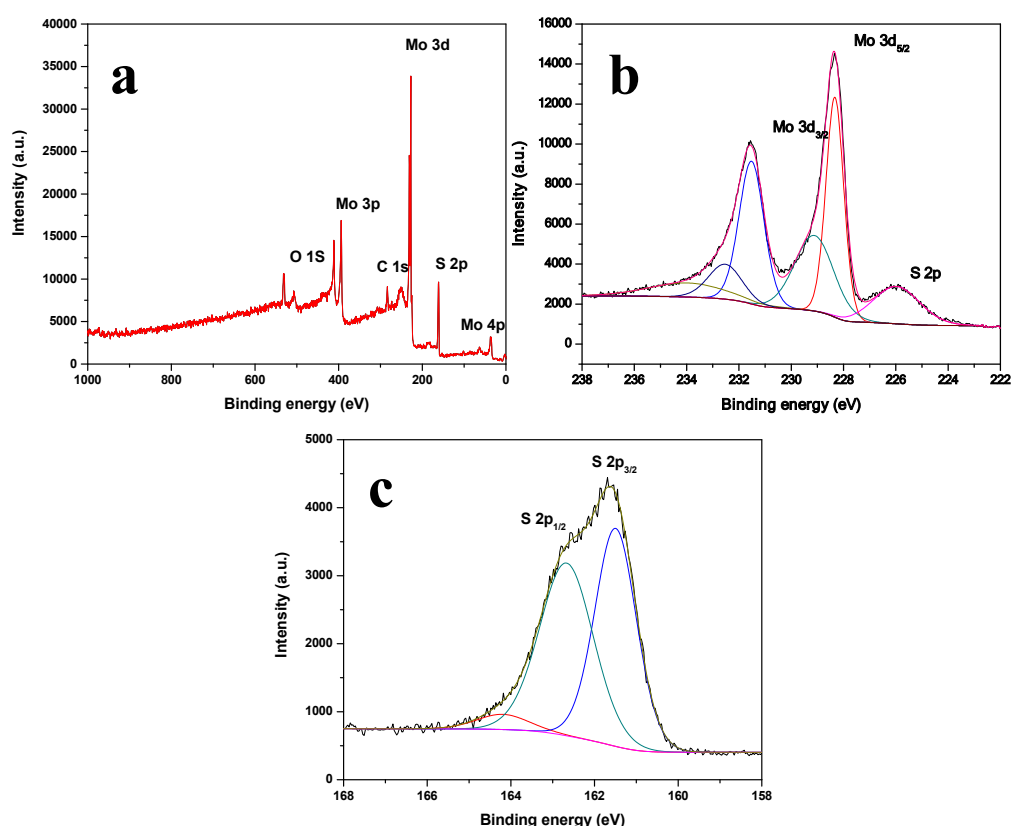


Figure S3: XPS spectra of V-MoS₂-TS, (a) survey spectra, (b) Mo 3d (c) S 2p.

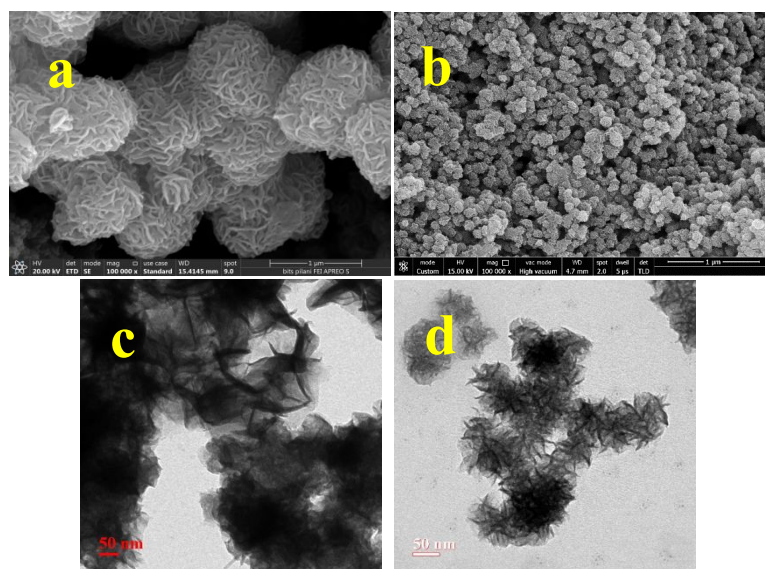


Figure S4: FESEM and TEM images of (a), (c), MoS₂-NS respectively and (b), (d) of MoS₂-TS respectively.

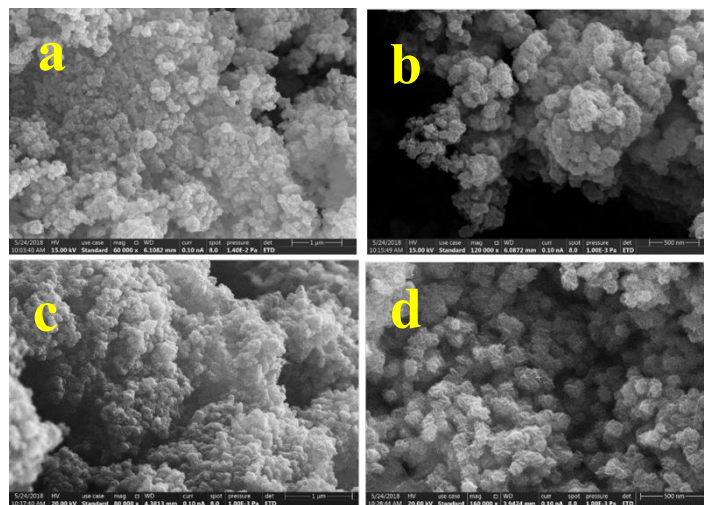


Figure S5: Low and High magnification FESEM images of (a,b) Cu-MoS₂-TS, (c,d) V-MoS₂-TS.

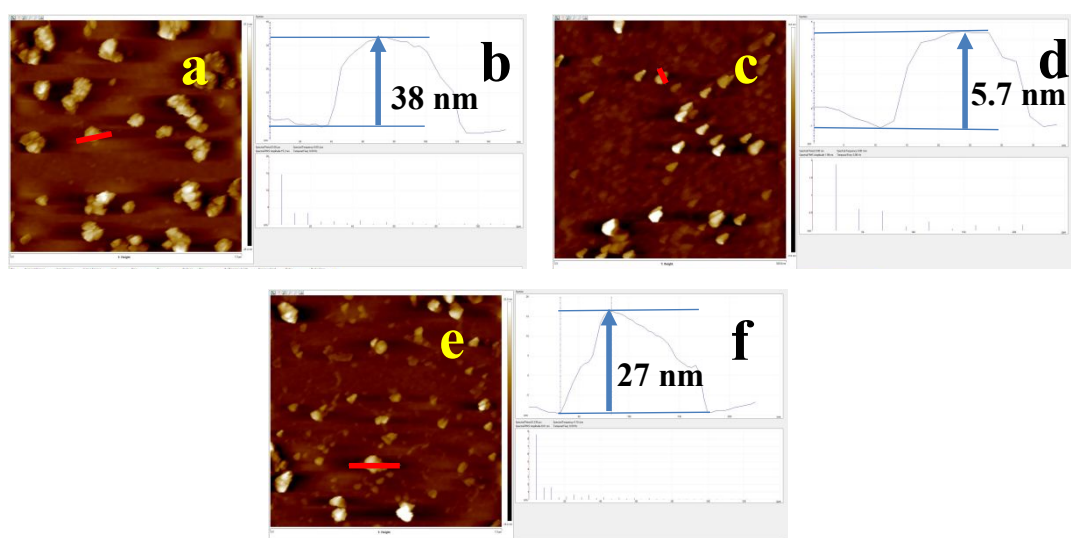


Figure S6: AFM images and corresponding height profile of (a,b) MoS₂-TS, (c,d) Cu-MoS₂-TS, (e,f) V-MoS₂-TS

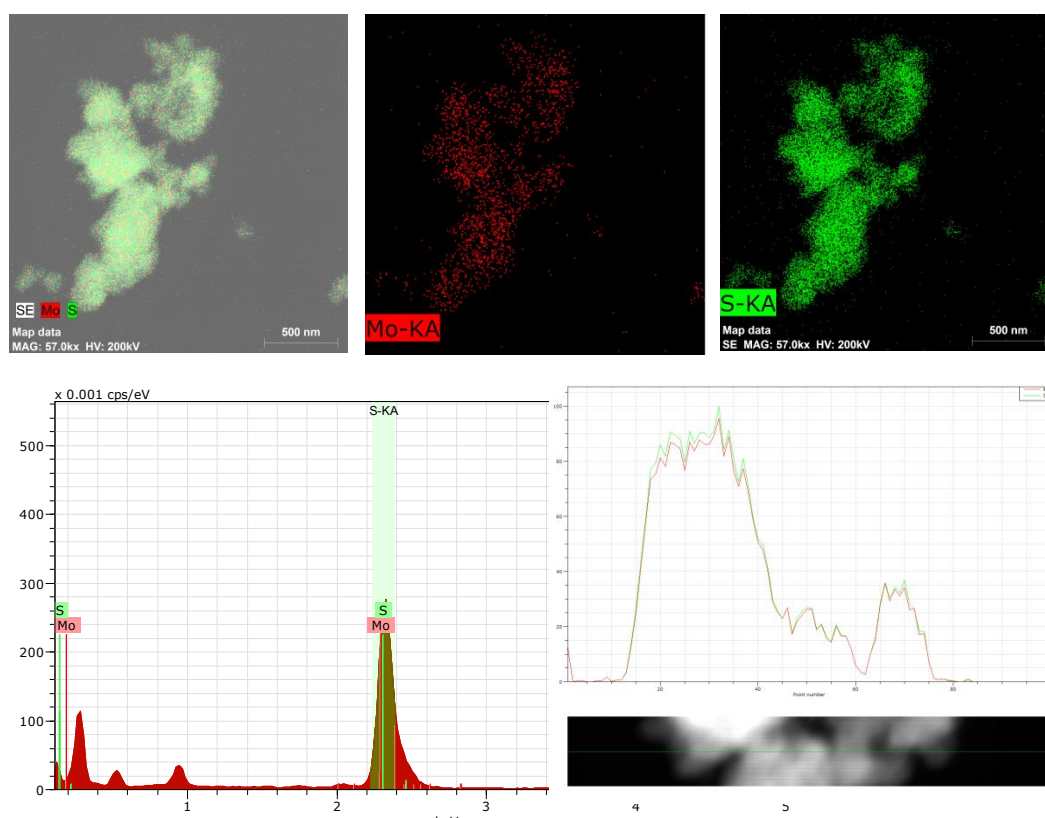


Figure S7: EDS mapping and EDS spectra of the MoS₂-TS.

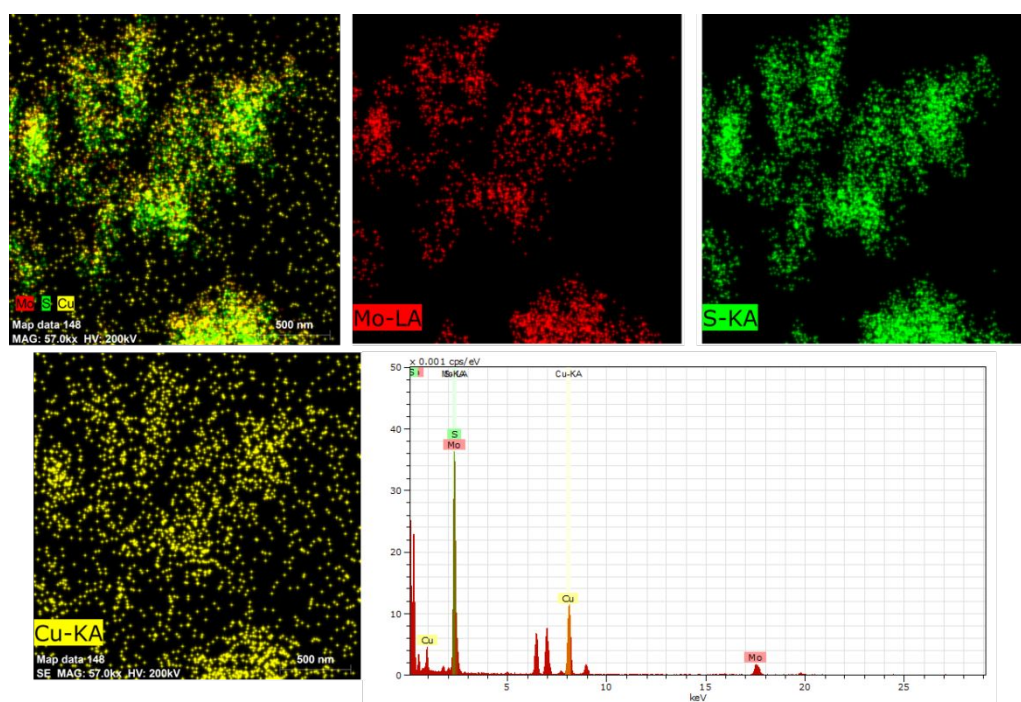


Figure S8: EDS mapping and EDS spectra of the Cu-MoS₂-TS.

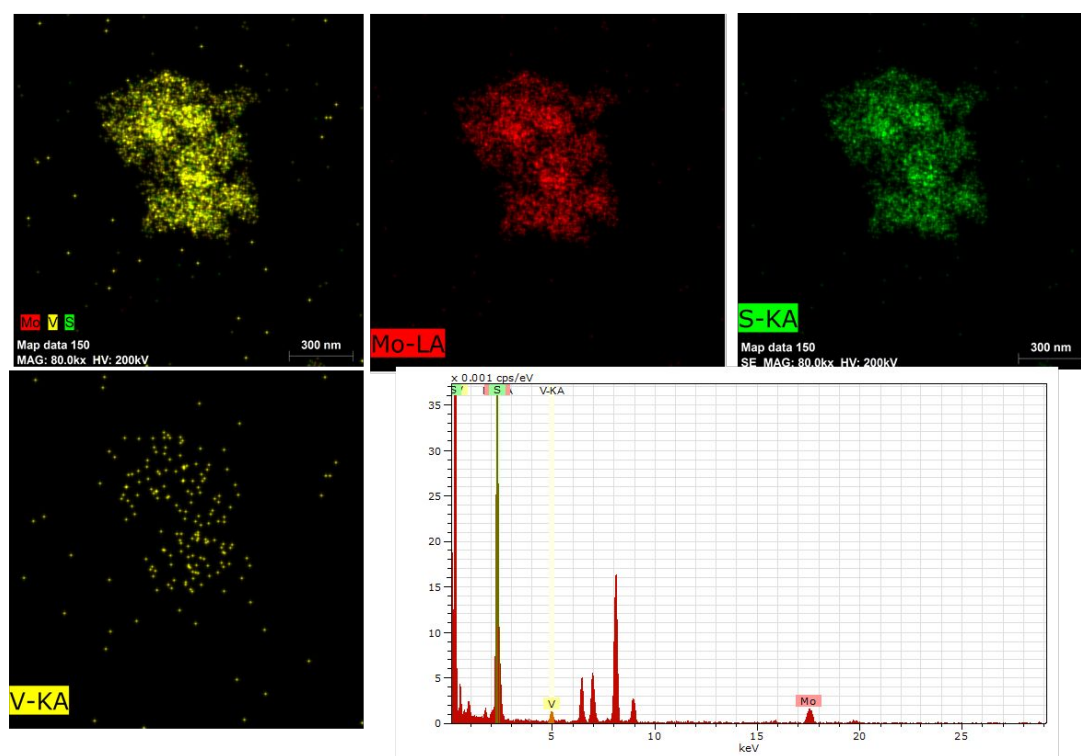


Figure S9: EDS mapping and EDS spectra of the V-MoS₂-TS.

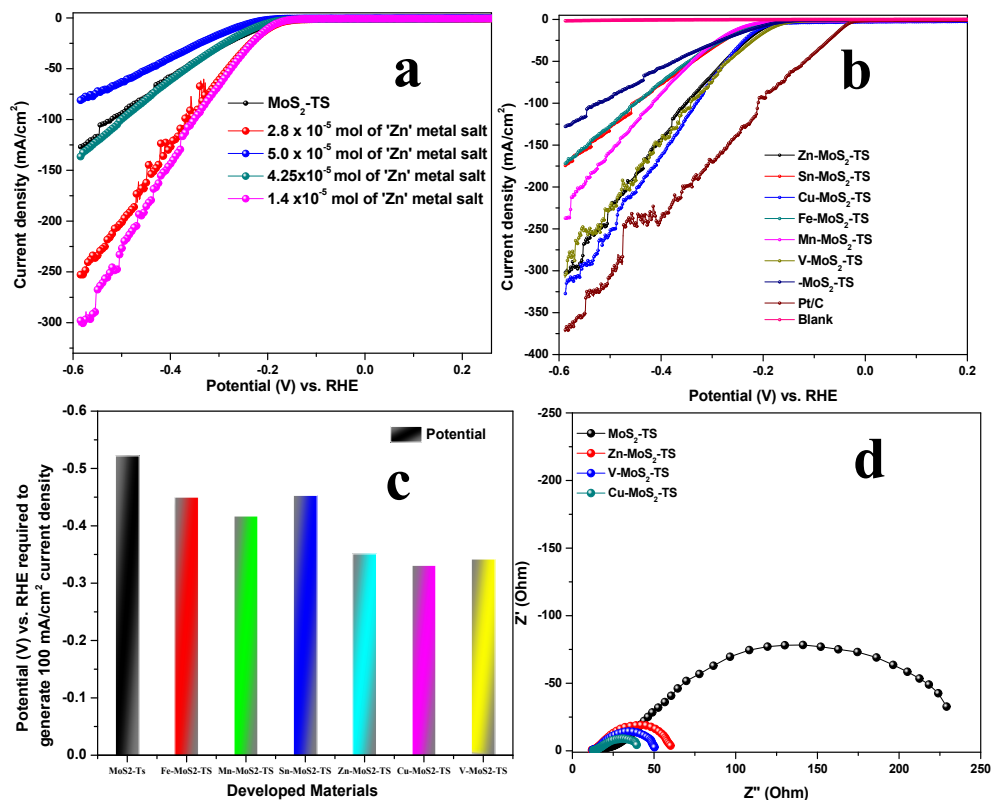


Figure S10: Comparative LSV plot of (a) doping of different concentration of 'Zn' metal precursor in MoS₂-TS and bare MoS₂-TS precursor metal, (b) all M doped MoS₂-TS (M = Zn, Sn, Cu, Fe, Mn, V), plot of variation in (c) Potential required to generate 100 mA/cm² current density, and (d) EIS Nyquist plot of all MoS₂-TS.

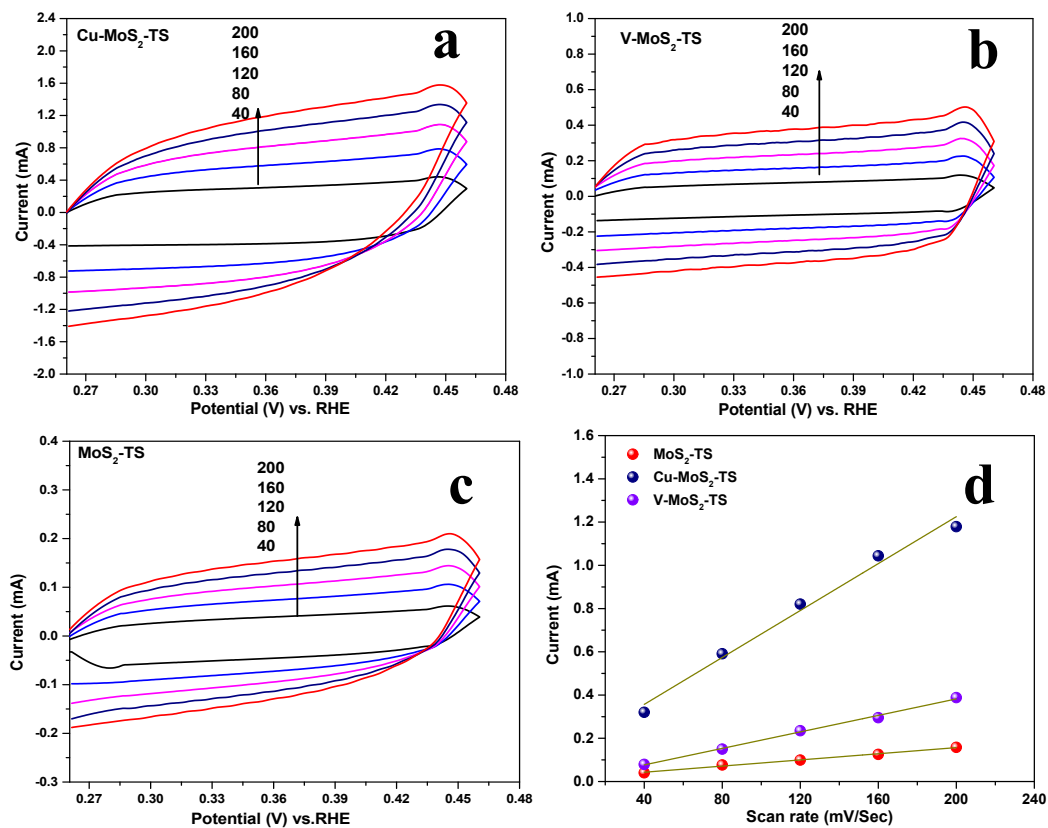


Figure S11: Cyclic voltammetry curves of (a) MoS₂-TS, (b) Cu-MoS₂-TS, (c) V-MoS₂-TS recorded in 0.5 M H₂SO₄ at scan rates of 40, 80, 120, 160 and 200 mV/s, and Plot of (d) capacitive current at 0.3605 V vs. RHE with scan rate.

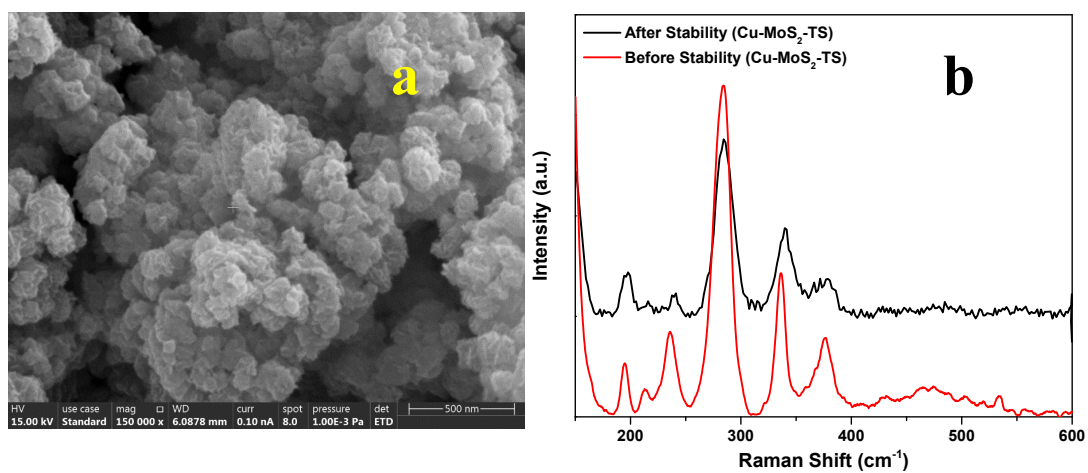


Figure S12: (a) FESEM image, (b) Raman spectra of Cu-MoS₂-TS after long term stability.

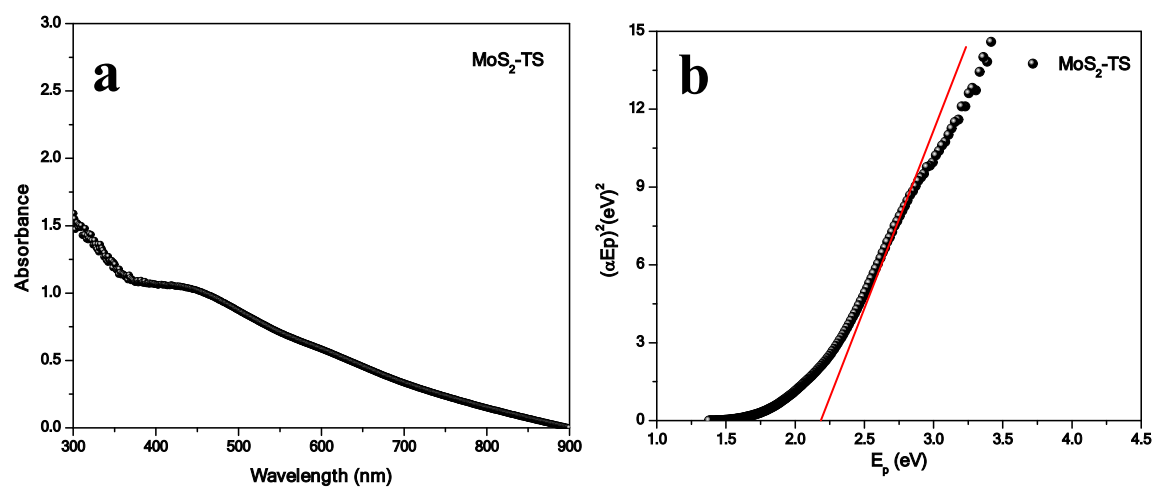


Figure S13: (a) UV-vis absorbance spectra, (b) plot of band gap determination of MoS₂-TS.

Table S1: ICP-OES analysis data

Synthesized Material	M (Atomic %) (Cu, V)	Mo (Atomic %)	M:Mo ratio
Cu-MoS ₂ -TS	0.008	0.045	1:6
V-MoS ₂ -TS	0.002	0.035	1: 17

Table S2: Comparative HER data for developed catalyst

Materials	Potential (V) to generate 50 mA/cm ² current density	Mass activity (A/g)	Tafel value (mV/decade)	ECSA (cm ²)
MoS ₂ -TS	-0.373	89.90	109.41	11.81
V-MoS ₂ -TS	-0.268	230.64	73.4	31.66
Cu- MoS ₂ -TS	-0.273	255.50	67.5	92.26
Pt/C (5%)	-0.118	370.18	—	—

Table S3: Comparative values of charge transfer resistance and solution resistance for all developed catalyst.

Cathode	R_s (Ohm)	R_{CT} (Ohm)
MoS ₂ - TS	24.42	165.3
Cu-MoS ₂ -TS	14.65	21.35
V-MoS ₂ -TS	14.37	32.46
Zn-MoS ₂ -TS	13.87	41.54
Fe-MoS ₂ -TS	17.39	37.38
Sn-MoS ₂ -TS	21.45	43.25
Mn-MoS ₂ -TS	34.01	21.21

Table S4: Comparative data of electrocatalytic activity of different reported catalysts, closely relating to the present work

Catalyst	Electrode reaction/Electrolyte	Overpotential (η) required to generate corresponding current density mV (mA/cm ²)	Tafel (mV/decade)	Ref.
MoS-C	HER/0.5 M H ₂ SO ₄	244(10)	71	R1
CoMoS-2-C		135 (10)	50	
MoS ₂	HER/0.5 M H ₂ SO ₄	518(10)	133	R2
Co _x Mo _{1-x} S ₂		357 (10)	120	
1T-MoS ₂	HER/0.5 M H ₂ SO ₄	-	135	R3
FeS ₂ doped MoS ₂ nanoflower		136 (10)	82	
Pristine MoS ₂	HER/0.5 M H ₂ SO ₄	300 (0.6)	118	25
Co doped MoS ₂		300 (3.6)	110	
Co(OH) ₂	OER/1.0 M KOH	350 (10)	47	27
Cu- Co(OH) ₂	OER/1.0 M KOH	300(10)	84	
CoS ₂	HER/0.5 M H ₂ SO ₄	327 (100)	87	28
Mn doped CoS ₂		103 (100)	34	
MoS ₂	HER/0.5 M H ₂ SO ₄	200 (3.6)	101	29
Zn doped MoS ₂		200 (49.5)	51	
MoS ₂	HER/0.5 M H ₂ SO ₄	200 (0.27)	135	R4
Mn-MoS ₂ /r-GO		200 (4.52)	76	
Fe-Ni(OH) ₂ /NiOOH	OER/1 M KOH	200 (10)	48	26
Ni(OH) ₂ /NiOOH		290 (10)	107	
Cu-MoS ₂ -TS	0.5 M H ₂ SO ₄	273 (50)	67.5	This work
V-MoS ₂ -TS		268 (50)	73.4	
MoS ₂ -TS		373 (50)	109.41	

R1: Dai, X.; Du, K.; Li, Z.; Liu, M.; Ma, Y.; Sun, H.; Zhang, X.; Yang, Y. Co-Doped MoS₂ Nanosheets with the Dominant CoMoS Phase Coated on Carbon as an Excellent Electrocatalyst for Hydrogen Evolution. *ACS Appl. Mater. Interfaces* **2015**, 7, 27242–27253.

R2: Pan, J.; Song, C.; Wang, X.; Yuan, X.; Fang, Y.; Guo, C.; Zhao, W.; Huang, F. Intermediate bands of MoS₂ enabled by Co doping for enhanced hydrogen evolution. *Inorg. Chem. Front.* **2017**, 4, 1895-1899.

R3: Zhao, X.; Maa, X.; Lua, Q.; Lia, Q.; Hana, C.; Xing, Z.; Yang, X.; FeS₂-doped MoS₂ nanoflower with the dominant 1T-MoS₂ phase as an excellent electrocatalyst for high-performance hydrogen evolution. *Electrochim. Acta* **2017**, 249, 72-78.

R4: Wu, L.; Xua, X.; Zhao, Y.; Zhang, K.; Sun, Y.; Wang, T.; Wang, Y.; Zhong, W.; Du, Y. Mn doped MoS₂/reduced graphene oxide hybrid for enhanced hydrogen evolution. *Appl Surf Sci.* **2017**, 425, 470-477.