Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Mo/Co Doped 1T-VS_2 Nanostructures as a Superior Bifunctional Electrocatalyst for Overall Water Splitting in Alkaline Media

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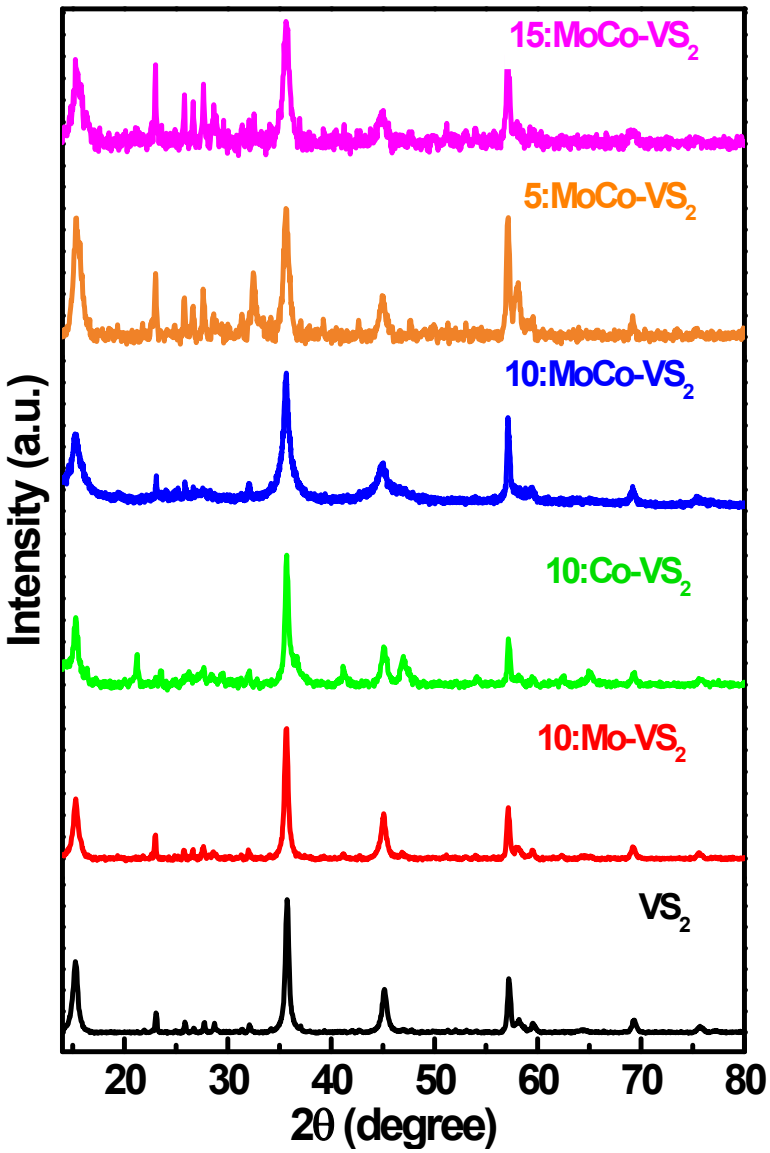

Fig. S1. XRD patterns of all samples.

Table S1: Structural parameters for as prepared samples estimated from XRD analysis

Parameters	(*hkl*)	VS_2 (JCPDS)	VS_2 (Obtained)	10:Mo-VS_2	10:Co-VS_2	10:MoCo-VS_2
2 θ (^{0})	001	15.384	15.251	15.321	15.295	15.250
	011	35.741	35.748	35.650	35.698	35.647
	012	45.237	45.148	44.951	45.098	45.05
	110	57.147	57.199	57.139	57.149	57.05
	103	58.329	58.197	58.101	58.150	58.005
	111	59.559	59.533	59.549	59.451	59.446
	201	69.259	69.314	69.199	69.347	68.999
	202	75.72	75.701	75.445	75.601	75.445
XRD peaks intensity (I)	001	83.3	2011	538	514	311
	011	100	3737	585	1110	460
	012	52	1206	185	303	120
	110	20.7	1515	544	390	318
	103	16.5	358.6	240	51.7	64.5
	111	6.6	238	84	71.5	50
	201	8.3	342.6	97	109	54.5
	202	6.9	159.6	35	51	26.5
'd' spacing (Å)	001	5.755	5.81	5.78	5.79	5.81
	011	2.51	2.51	2.52	2.52	2.52
	012	2.003	2.01	2.02	2.01	2.01
	110	1.611	1.61	1.61	1.61	1.61
	103	1.581	1.59	1.59	1.59	1.59
	111	1.551	1.55	1.55	1.55	1.55
	201	1.356	1.36	1.36	1.36	1.36
	202	1.255	1.26	1.26	1.26	1.26
FWHM β (radians) x 10^{-3}			6.7	10.3	6.9	11.5
Avg. Crystallite			21.5	14.18		12.67

size D (nm)				21.1	
Dislocation density 'δ' (lines/m^2) x 10^{14}		22	49.7	21.6	62
Texture coefficient (TC)	001	0.6897	0.6	0.6461	0.6236
	011	1.0677	0.5435	1.1623	0.7684
	012	0.6626	0.3305	0.6101	0.3854
	110	2.091	2.4418	1.9728	2.5663
	103	0.6209	1.3515	0.3281	0.653
	111	1.0303	1.1825	1.1343	1.2655
	201	1.1771	1.0858	1.3751	1.0969
	202	0.66	0.4645	0.7739	0.6415
Micro strain 'ε'		0.005 %	0.008 %	0.005 %	0.009 %

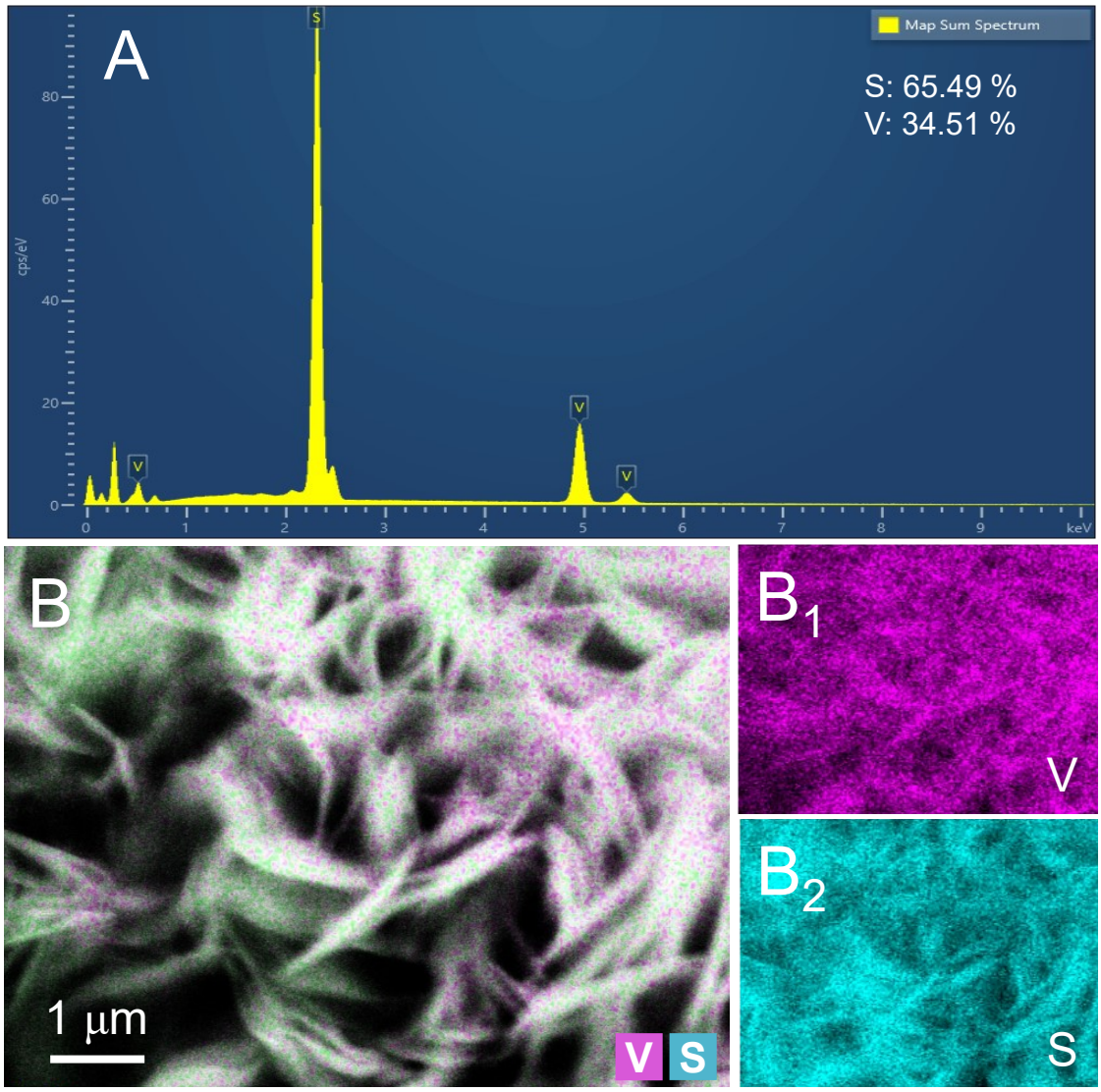

Fig. S2. Energy dispersive X-ray spectroscopy (EDX) analysis of 1T-VS_2/CC **(A)** EDX spectrum, **(B)** EDX layered image, elemental mapping corresponds to (B_1) Vanadium and (B_2) S elements.

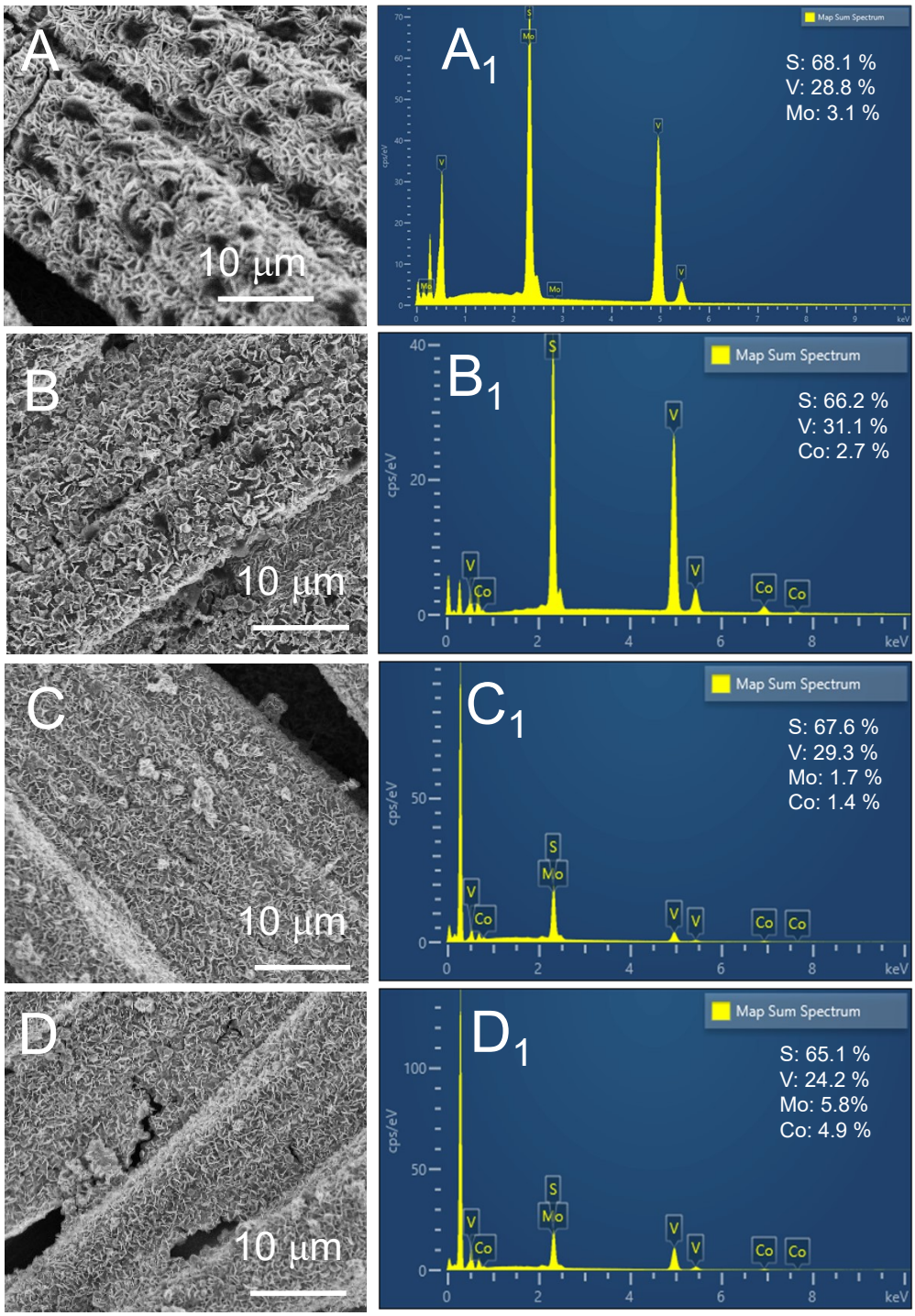

Fig. S3. (A-D) FESEM images of 10:Mo-VS_2/CC, 10:Co-VS_2/CC, 5:MoCo-VS_2/CC and 15:MoCo-VS_2/CC, and their respective EDX spectrum.

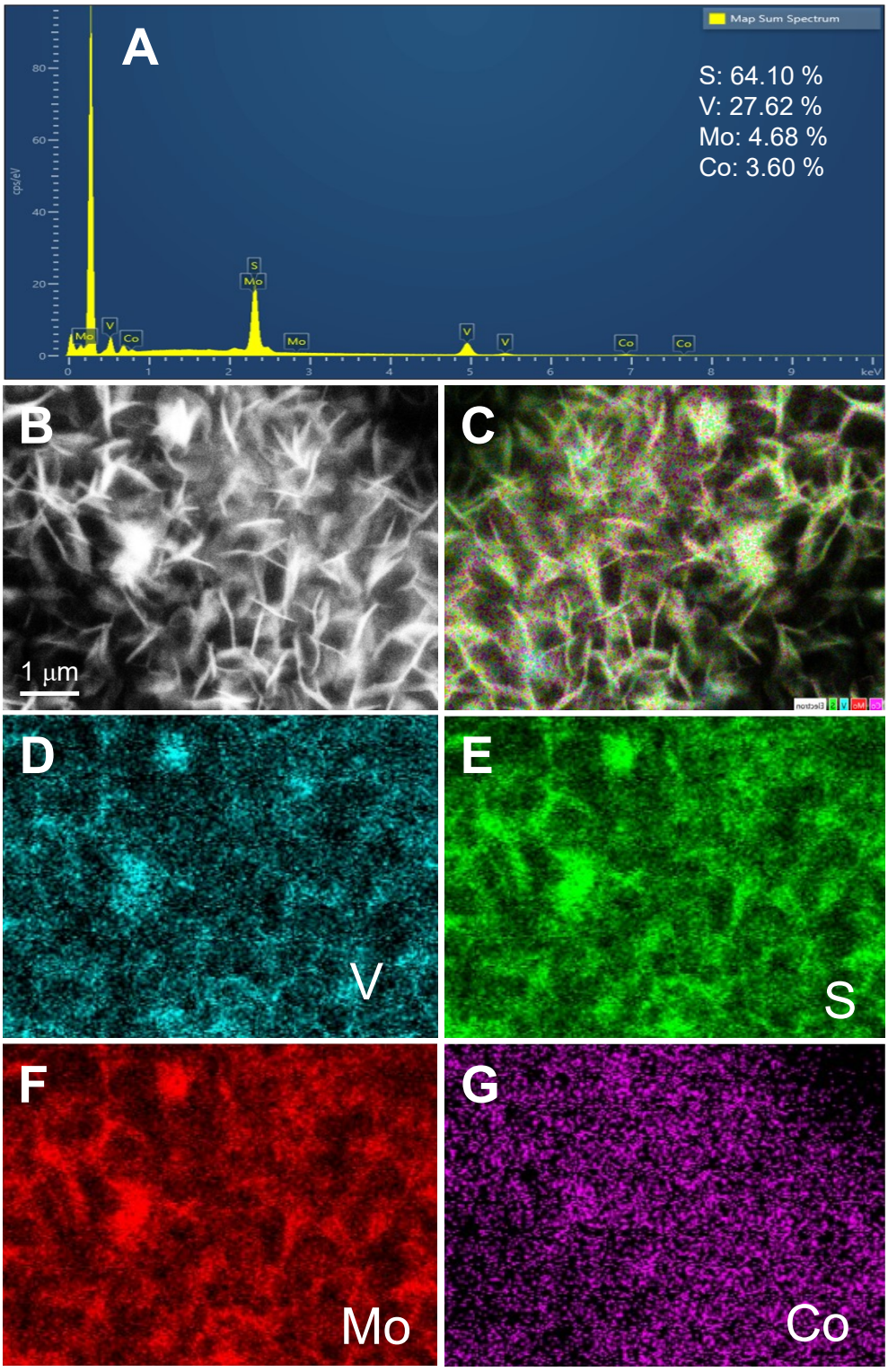

Fig. S4. Energy dispersive X-ray spectroscopy (EDX) analysis of 10:MoCo-VS_2/CC: **(A)** EDX spectrum, **(B)** Electron image, **(C)** EDX layered image, and **(D-G)** Elemental mapping corresponding to constituent elements: Vanadium (V), Sulfur (S), Molybdenum (Mo) and Cobalt (Co).

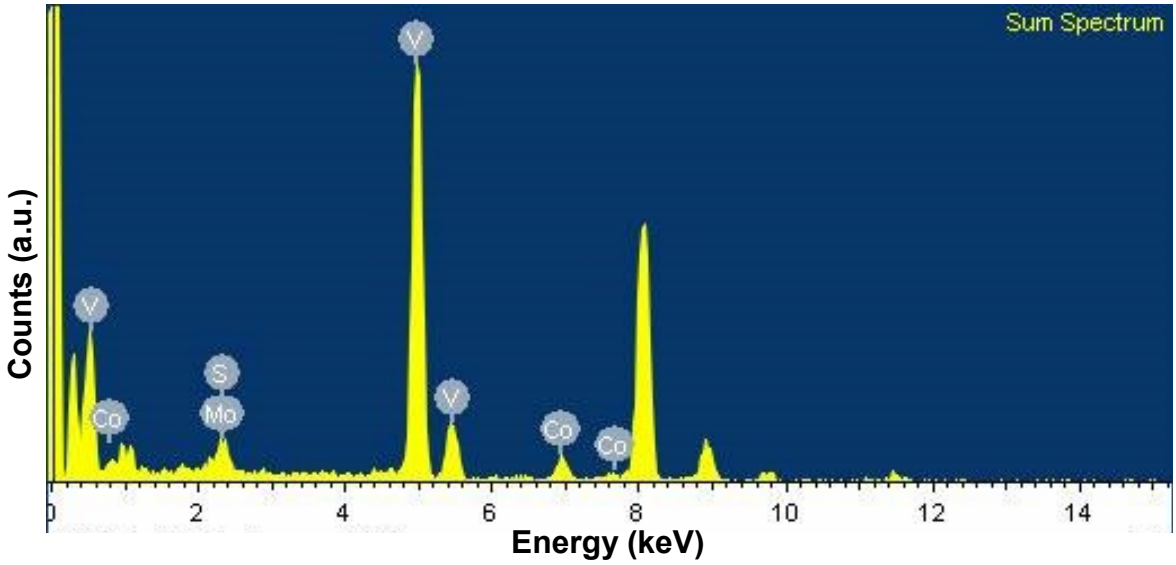

Fig. S5. EDX spectrum of 10:MoCo-VS_2 sample.

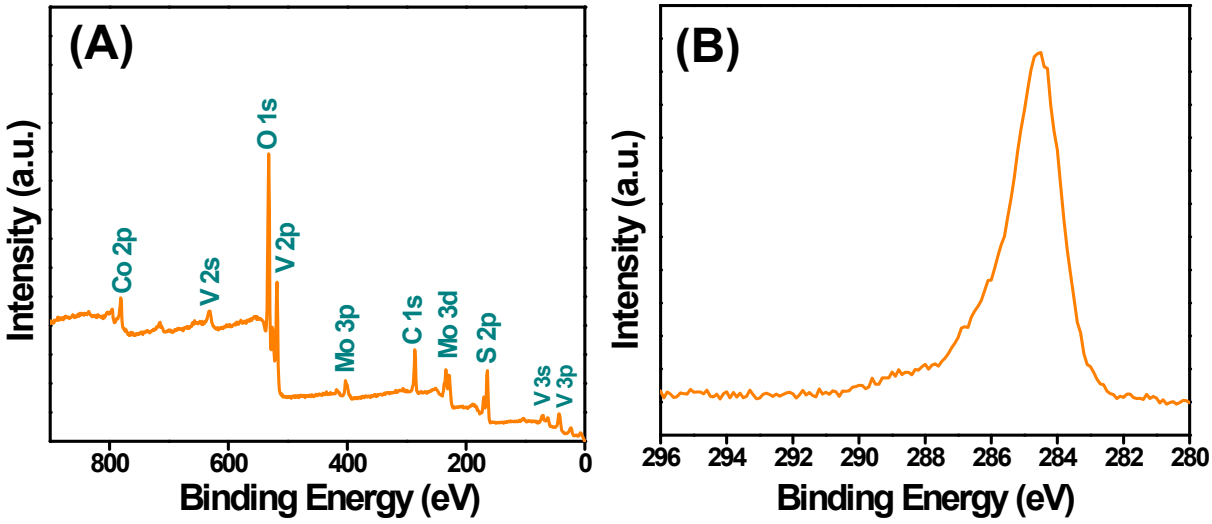

Fig. S6. (A) XPS survey spectrum and (B) high resolution C 1s spectrum of 10:MoCo-VS2/CC (1T-$V_{0.8}Mo_{0.1}Co_{0.1}S_2$/CC) sample.

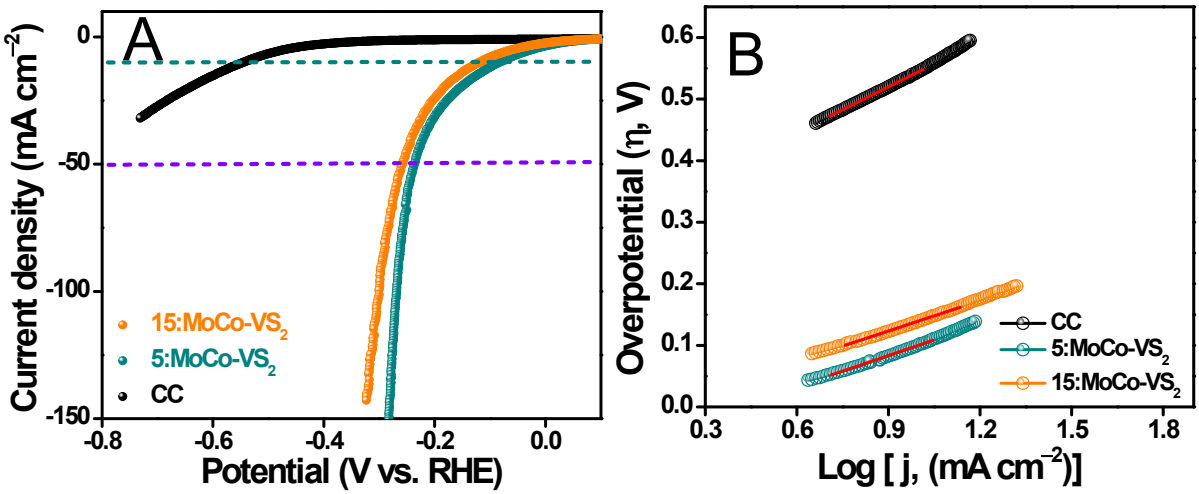

Fig. S7. (A) Linear–sweep voltammetry (LSV) curves for HER of the bare carbon cloth, and all other catalysts on carbon cloth, (B) Tafel plots of electrocatalysts.

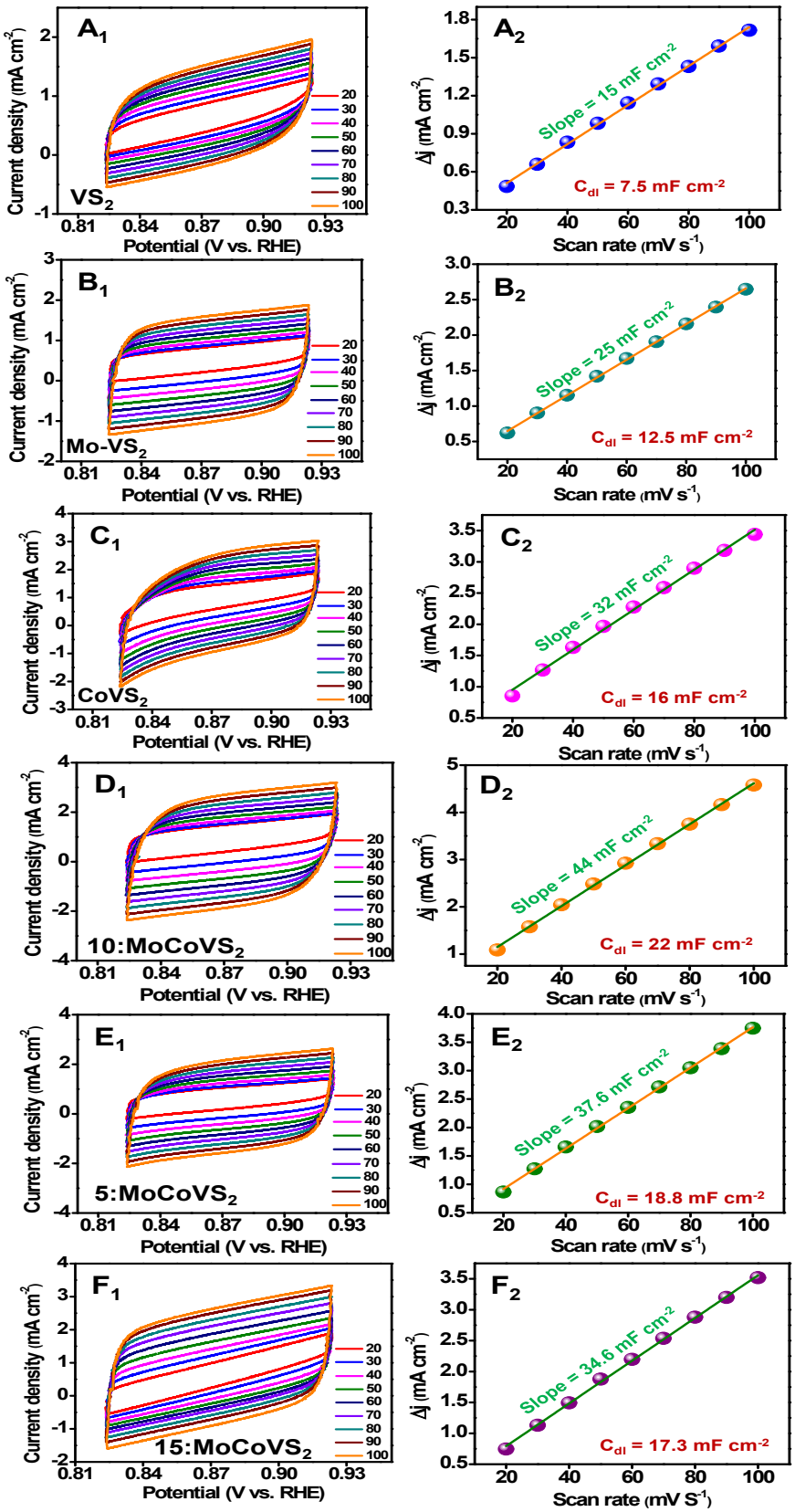

Fig. S8. (A_1-F_1) Cyclic voltammograms of various catalysts recorded at different scan rates ranging from 20-100 mV s^{-1}, and (A_2-F_2) plot of current density with scan rates of corresponding samples.

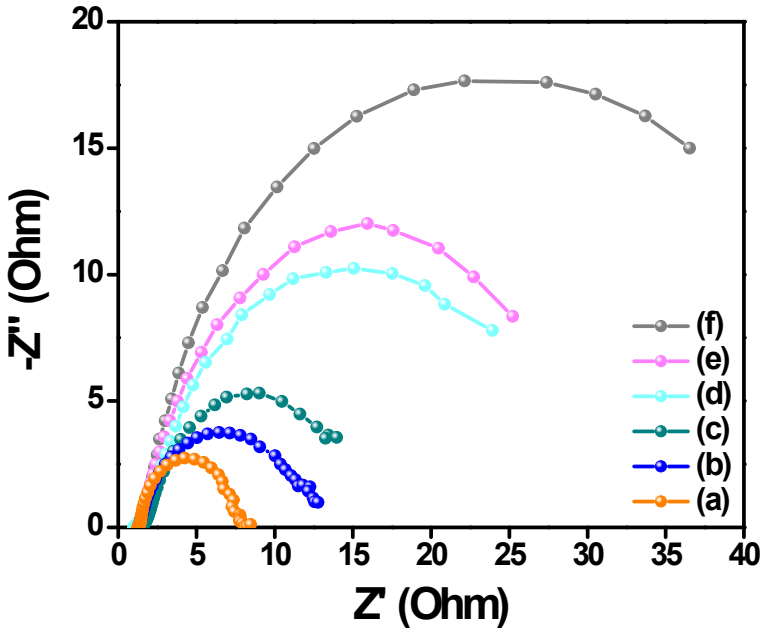

Fig. S9. Electrical impedance spectra (EIS) of **(a)** 10:MoCo-VS_2/CC, **(b)** 5:MoCo-VS_2/CC, **(c)** 15:MoCo-VS_2/CC, **(d)** 10:Co-VS_2/CC, **(e)** 10:Mo-VS_2/CC, **(f)** VS_2/CC.

Turnover Frequency (TOF) Calculation:

The per-site turnover frequency for HER and OER were calculated using the following formulae.

(i) For HER:

$$TOF = \frac{\#total\ hydrogen\ turn\ overs/cm^2\ geometric\ area}{\#surface\ sites/cm^2\ geometric\ area} \quad \text{(i)}$$

The total number of hydrogen turn overs can be obtained from the current density as below

$$\#H_2 = \left(j\frac{mA}{cm^2}\right)\left(\frac{1\ Cs^{-1}}{1000\ mA}\right)\left(\frac{1\ mol\ e^-}{96485.3\ C}\right)\left(\frac{1\ mol\ H_2}{2\ mol\ e^-}\right)\left(\frac{6.022\times10^{23}\ H_2\ molecules}{1\ mol\ H_2}\right)$$

$$\#H_2 = \left(j\frac{mA}{cm^2}\right)\times 3.12\times10^{15}\frac{H_2/s}{cm^2} \quad \text{(ii)}$$

where j values corresponding to overpotential of 100 mv for different electrocatalysts have been taken from the HER LSV curve.

Since the exact hydrogen binding sites are not known, so we can estimate the number of active sites as the total number of surface sites by assuming both the transition metal and S atoms as possible active sites.

$$\#surface\ sites = \left(\frac{3\ atoms/unit\ cell}{unit\ cell\ volume}\right)^{\frac{2}{3}} = 1.39\ \times 10^{15}\ atoms\ cm^{-2} \quad \text{(iii)}$$

where unit cell volume is 57.75 Å^3 (lattice parameters of VS_2: a = 3.1939 Å, b = 3.1939 Å, c = 6.5376 Å.

(ii) For OER:

$$TOF_{avg} = \frac{\#total\ oxygen\ turn\ overs/cm^2\ geometric\ area}{\#surface\ sites/cm^2\ geometric\ area} \quad \text{(iv)}$$

The total number of oxygen turn overs can be obtained from the current density as below

$$\#O_2 = \left(j\frac{mA}{cm^2}\right)\left(\frac{1\ Cs^{-1}}{1000\ mA}\right)\left(\frac{1\ mol\ e^-}{96485.3\ C}\right)\left(\frac{1\ mol\ O_2}{4\ mol\ e^-}\right)\left(\frac{6.022 \times 10^{23}\ O_2\ molecules}{1\ mol\ O_2}\right)$$

$$\#O_2 = \left(j\frac{mA}{cm^2}\right) \times 1.56 \times 10^{15}\frac{O_2/s}{cm^2} \quad \text{(v)}$$

where j values corresponding to overpotential of 320 mv for different electrocatalysts have been taken from the OER LSV curve. The value of #surface site in equation (iv) is plugged from equation (iii).

Table S2: TOF values of all the electrocatalysts.

Sample	TOF_{HER}	TOF_{OER}
VS_2	0.031338136	0.001966104
10: Mo-VS_2	0.009107422	0.007859633
10: Co-VS_2	0.007540963	0.06448756
5: MoCo-VS_2	0.056764039	0.171476987
10: MoCo-VS_2	0.057614059	0.184874306
15: MoCo-VS_2	0.041628184	0.108459192

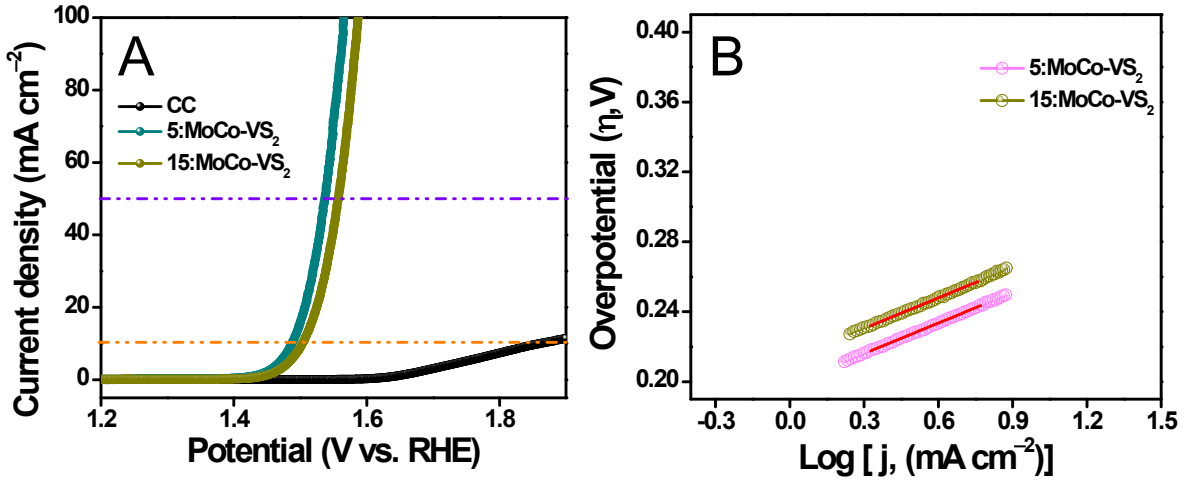

Fig. S10. (A) Linear–sweep voltammetry (LSV) curves for OER of bare carbon cloth and other catalysts on carbon cloth, (B) Tafel plots of electrocatalysts.

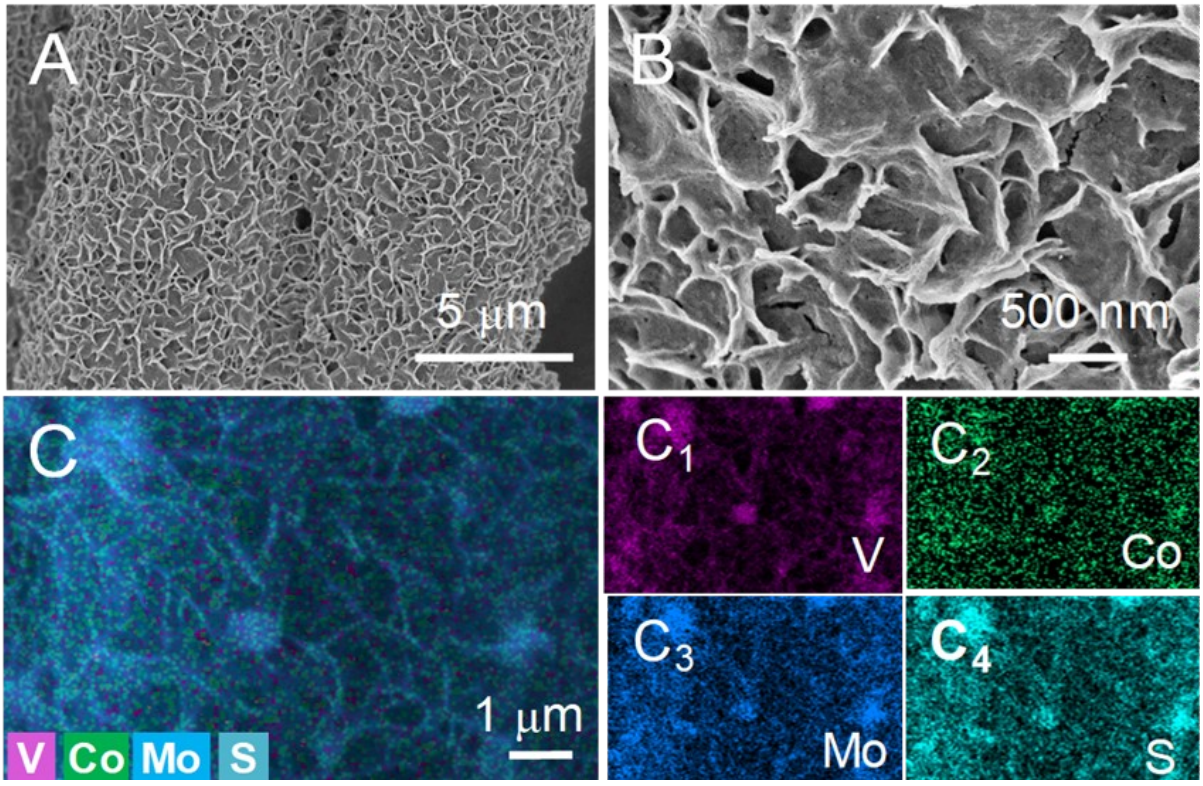

Fig. S11. (A-B) FESEM images at different magnifications, **(C)** EDX layered image, **(C1-C4)** elemental mappings corresponding to V, Co, Mo and S atoms showing nominal changes

in morphology of electrode materials after the long-term chronoamperometric stability test of the device.

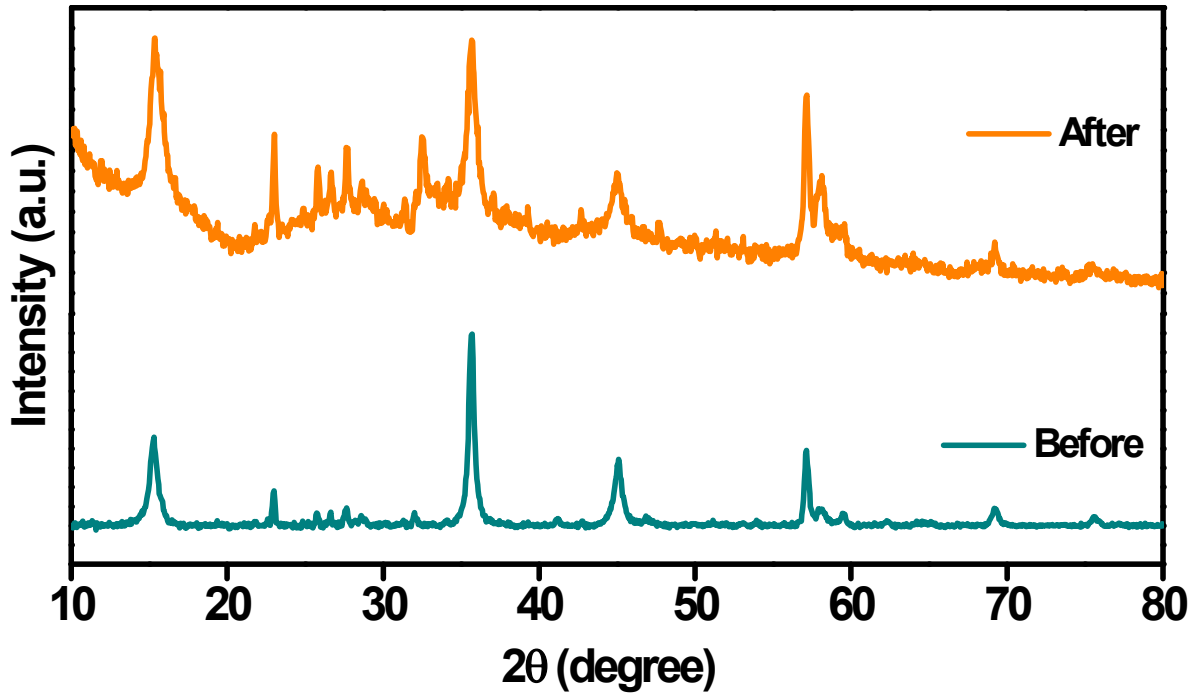

Fig. S12. XRD spectra of 10:MoCo-VS2 electrocatalyst before and after the electrochemical test.

Table S3. Comparison of HER performance of recently reported catalysts.

Catalyst	**HER Overpotential η (mV) for J = 10 $mAcm^{-2}$**	**Tafel Slope ($mV\ dec^{-1}$)**	**Reference**
VS_2	922	305.4	[1]
VS_2 nanoflowers	58	34	[2]
VS_2	68	34	[3]
VS_2 nanoplates	42	36	[4]
Mo-VS_2	243	52.6	[1]
VS_2@MoS_2	97	54.9	[5]
VS_2 nanosheets	43	36	[6]
10:MoCo-VS_2/CC	**63**	**50**	**Present Work**

Table S4. Comparison of the OER performance of recently reported catalysts.

Catalyst	OER Overpotential (mV)	Tafel Slope (mV dec^{-1})	Reference
MoS_2/Ni	310 (@20 mA cm^{-2})	105	[7]
MoS_2-QD	370 (@ 10 mA cm^{-2})	39	[8]
Co-MoS_2/BCCF-21	260 (@ 10 mA cm^{-2})	85	[9]
Co_2VO_4	300 (@ 10 mA cm^{-2})	65.32	[10]
Ni_3S_2/VS_2	227 (@ 10 mA cm^{-2})	59.9	[11]
NiFe(OH)x/VS/NF NSs	276 (@200 mA cm^{-2})	75	[12]
V-Ni_3S_2@NiO/NF	310 (@ 100 mA cm^{-2})	98.8	[13]
1T-$V_{0.8}Mo_{0.1}Co_{0.1}S_2$/CC	**248 (@ 10 mA cm^{-2})**	**55**	**Present work**

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