Supporting Information for Publication

Vacancy Fused Multiple Layers of Copper Sulfoselenide Superstructures: A Propitious HER Electrocatalyst in Acidic Medium

Sangeetha Kumaravel,[†‡] Dhirendra Kumar,[$,] Selvasundarasekar Sam Sankar,[†‡] Arun Karmakar [†‡] Ragunath Madhu,[†‡] Krishnendu Bera,[†‡] Hariharan N Dhandapani,[†‡] Sreenivasan Nagappan,[†‡] Sudip Chakraborty,[$,*] and Subrata Kundu[†‡*]

[†] *Electrochemical Process Engineering (EPE) Division, CSIR-Central Electrochemical Research Institute (CECRI), Karaikudi-630003, Tamil Nadu, India.*

[‡] *Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India.*

[$] *Materials Theory for Energy Scavenging (MATES) Lab, Harish-Chandra Research Institute, A CI of Homi Bhabha National Institute, Chhatnag Road, Jhunsi, Prayagraj-211019, India.*

*To whom correspondence should be addressed, *E-mail: skundu@cecri.res.in; kundu.subrata@gmail.com and sudipchakraborty@hri.res.in;* Tel: +91 4565-241487.

This file contains pages from S1 to S27, where the detailed, reagents and instruments used in the study, figures and Tables corresponding to Cu_2S-Se has been given.

Number of Pages: 27

Number of Figures: 18

Number of Tables: 01

Instruments used in the studies

Before and after selenization, the four set of catalyst such as CuS-Wet, CuS-Hyd, CuS-Se-Wet and CuS-Se-Hyd was characterized using the techniques such as XRD, FE-SEM, HR-TEM, EDS, HAADF, EPR and XPS analysis. The X-ray diffraction (XRD) analysis was carried using a PAN analytical Advanced Bragg-Brentano X-ray powder diffractometer (XRD) with Cu K_α radiation (λ = 0.154178 nm) with a scanning rate of 0.020 s^{-1} in the 2θ range 10-80°. The morphological studies and the HAADF color mapping of both the electrocatalyst was carried in HR-TEM, (TecnaiTM G2TF20) working at an accelerating voltage of 200 kV. The Energy Dispersive X-ray Spectroscopy (EDS) analysis was done with the HR-TEM with a separate EDS detector (INCA) connected to that instrument. The X-ray photoelectron spectroscopic (XPS) analysis was done to check the state of elements present in the outermost part of materials and analyzed by using Theta Probe AR-XPS System, Thermo Fisher Scientific (U.K). The Electron ParaMagnetic Resonance (EPR) Spectroscopy, was performed in EMX Plus X Band with the software of Bruker WIN EPR Acquisition and Processing and the source used are microwaves. Further, the Field Emission Scanning Electron Microscope (FE-SEM) analysis was performed using SUPRA 55VP, Gemini Column with air lock system (Carl Zeiss, Germany). The entire HER study was carried out using Aut-M204 instrument. SCE (reference electrodes) was purchased from the Aut-M204 auto-lab instrument and the Pt (counter electrode) were purchased from Alfa- Aesar.

Materials used and sample preparation for various characterizations

For the preparation of Cu_2S and Cu_2S-Se, the precursor used are sodium sulfide (Na_2S) (98%), selenium (Se) metal powder (99.99%) and Sodium borohydride ($NaBH_4$) (98%) was purchased from Sigma-Aldrich. Also, the Cu foam was procured from Alfa-aesar. The deionized water (DI) has been used for the complete study. After the formation of the catalyst, the various characterization studies were carried out such as XRD, FE-SEM, HR-TEM, EDS, HAADF, EPR and XPS analysis. For XRD, FE-SEM, EPR, and XPS analysis, the as prepared electrodes were directly taken for the studies. For HR-TEM, EDS and HAADF colour mapping, the catalyst such as Cu_2S and Cu_2S-Se developed over Cu foam was sonicated in DI water for 1 hour and the solution was straight away dropped over the copper coated carbon grid followed by steady evaporation at room temperature. The same has been studied for EDS and HAADF colour mapping with the separate detector system with the HR-TEM instrument.

Mass activity calculation

Current observed in particular potential for the for Cu_2S-Wet, Cu_2S-Hyd, Cu_2S-Se-Wet and Cu_2S-Se-Hyd catalysts

Mass loading calculated for **Cu_2S-Wet and Cu_2S-Hyd** = 0.1 mg cm^{-2}

Mass loading calculated for **Cu_2S-Se-Wet and Cu_2S-Hyd** = 0.2 mg cm^{-2}

Fixed Overpotential (V)	**Current density of Cu_2S-Wet in mA cm^{-2}**	**Current density of Cu_2S-Hyd in mA cm^{-2}**	**Current density of Cu_2S-Se-Wet in mA cm^{-2}**	**Current density of Cu_2S-Se-Hyd in mA cm^{-2}**
-0.3	-3.94	-3.96	-64.657-	-20.147
-0.35	-8.0	-8.0	-198.189	-60.611
-0.4	-37.551	-25.64	-534.352	-145.897

Mass activity is calculated using the formulae,

Mass activity = Current density/Loading of a catalyst

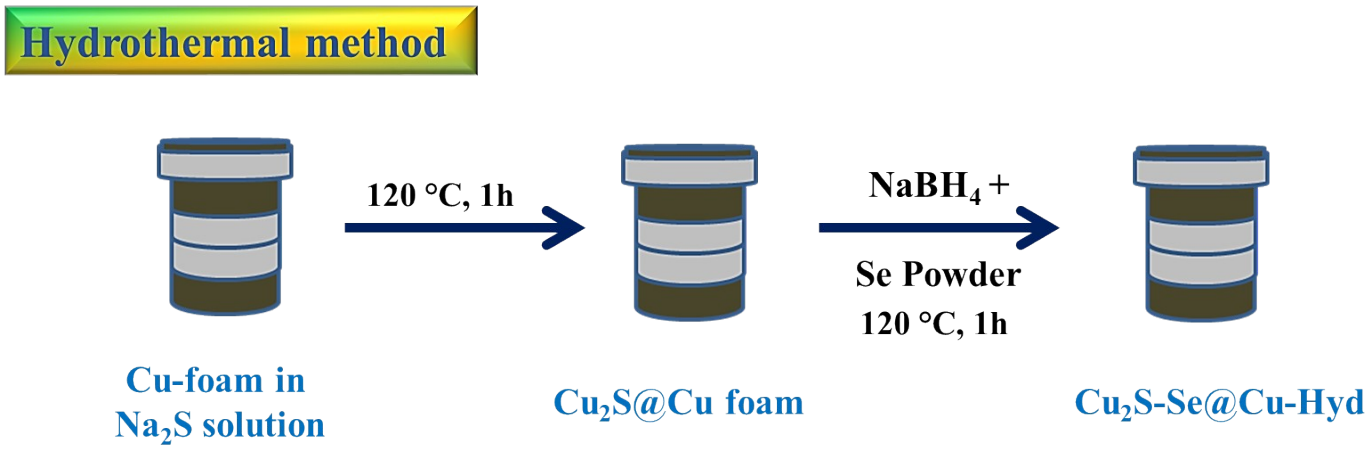
Hence, the mass activity calculated all the four catalyst at high current density **-0.4 V**,

Mass activity calculated = -37.551/0.1 = 375.51 mA/mg cm^{-2} for **Cu_2S-Wet**

Mass activity calculated = -25.64/0.1 = 25.64 mA/mg cm^{-2} for **Cu_2S-Hyd**

Mass activity calculated = -534.352/0.2 = 2674.76 mA/mg cm^{-2} for **Cu_2S-Se-Wet**

Mass activity calculated = -145.897/0.2 = 734.485 mA/mg cm^{-2} for **Cu_2S-Se-Hyd**



Scheme S1. *Synthesis scheme involves the formation of Cu_2S and Cu_2S-Se by following hydrothermal methods.*

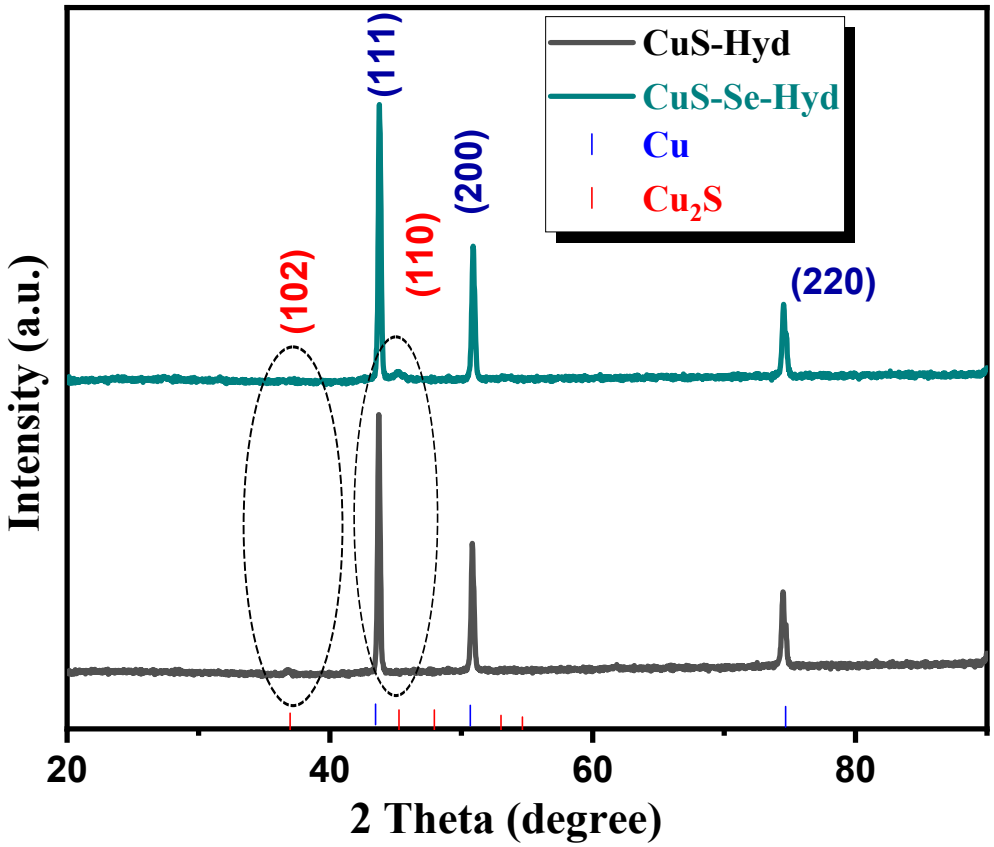


Figure S1. *Stacked XRD pattern of hydrothermally prepared Cu_2S@Cu foam and Cu_2S-Se@Cu foam and (b) Zoomed XRD pattern of the same indicating the shift after selenization.*

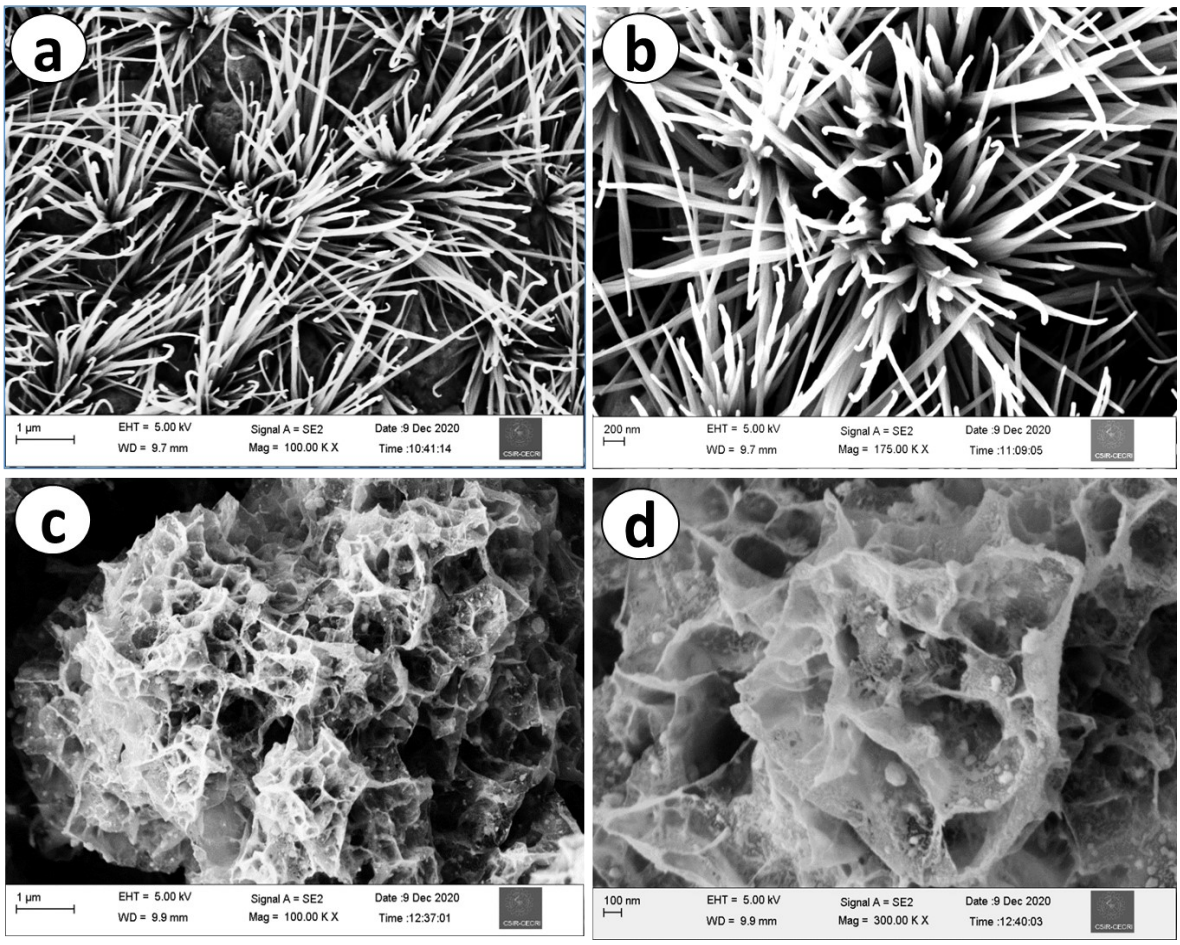


Figure S2. *(a and b) Low and high magnified FE-SEM images of hydrothermally prepared Cu_2S nano-needles and (c and d) Low and high magnified images of layered Cu_2S-Se-Hyd sample.*

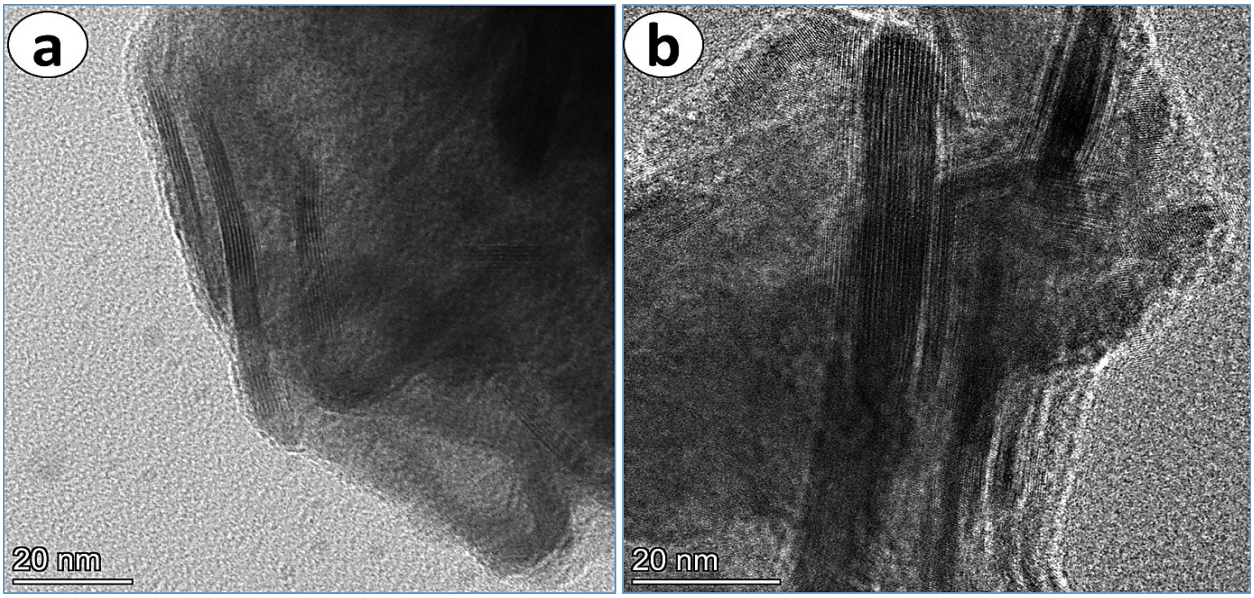


Figure S3. *The HR-TEM image of layered structure of Cu_2S-Se-Wet.*

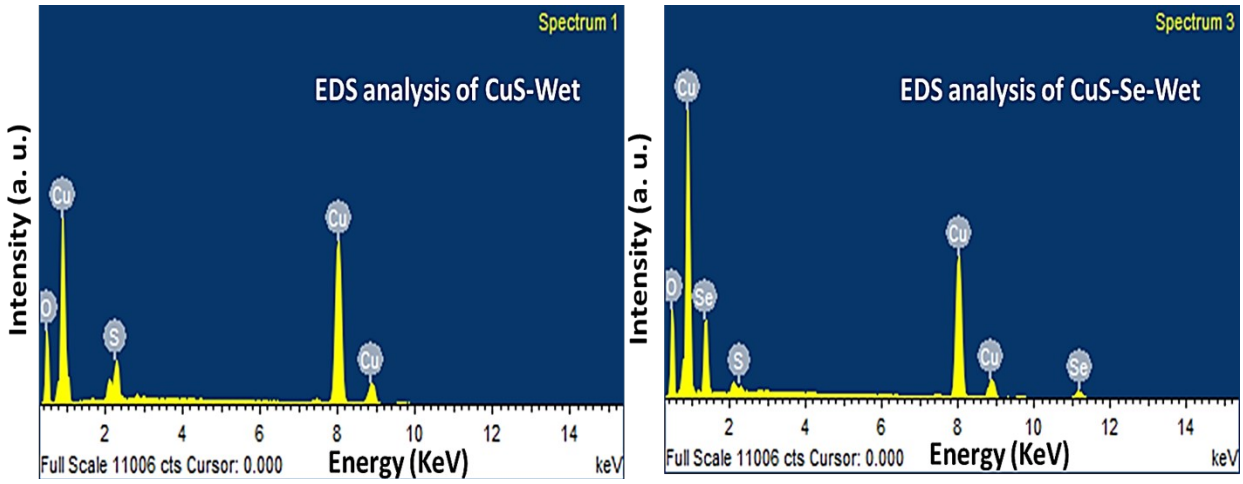


Figure S4. *EDS analysis of the wet-chemically prepared samples such as Cu_2S-Wet and Cu_2S-Se-Wet.*

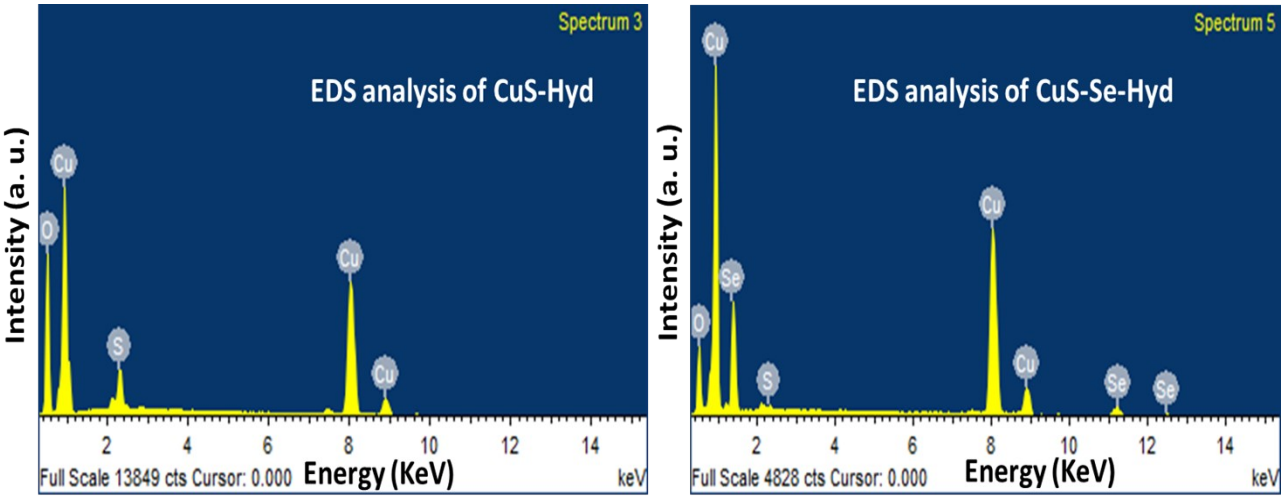


Figure S5. *EDS analysis of the hydrothermally prepare samples such as Cu_2S-Hyd and Cu_2S-Se-Hyd.*

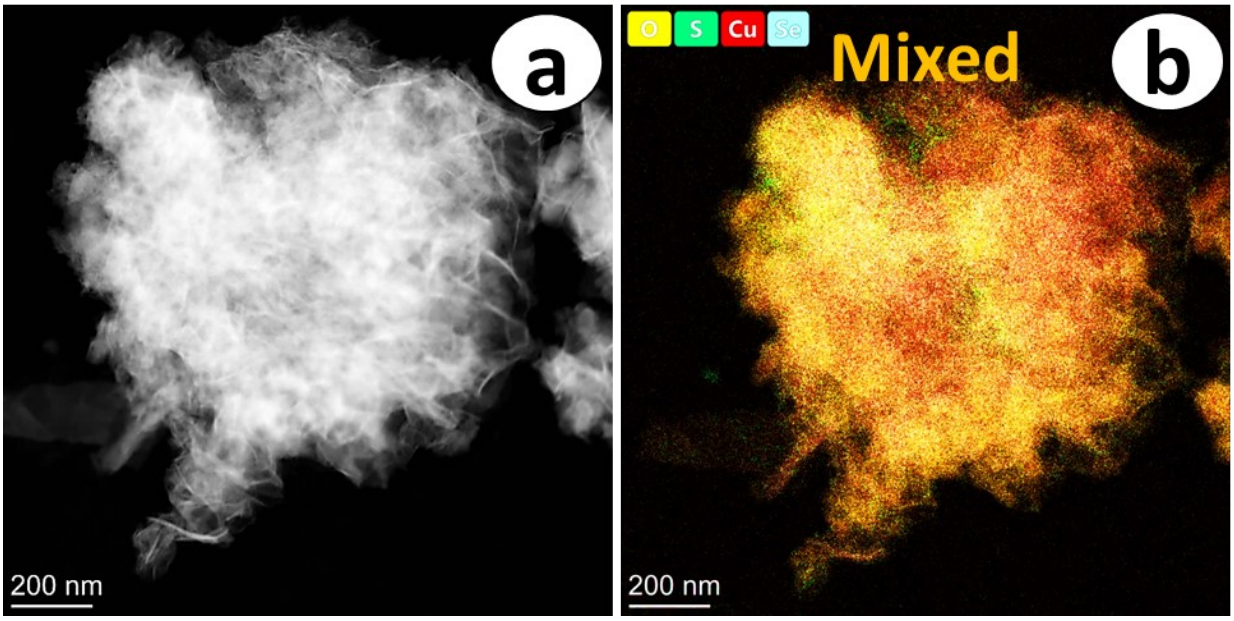


Figure S6. *(a) HR-TEM image of layered Cu_2S-Se-Wet and (b) mixed HAADF elemental mapping of Cu_2S-Se-Wet.*

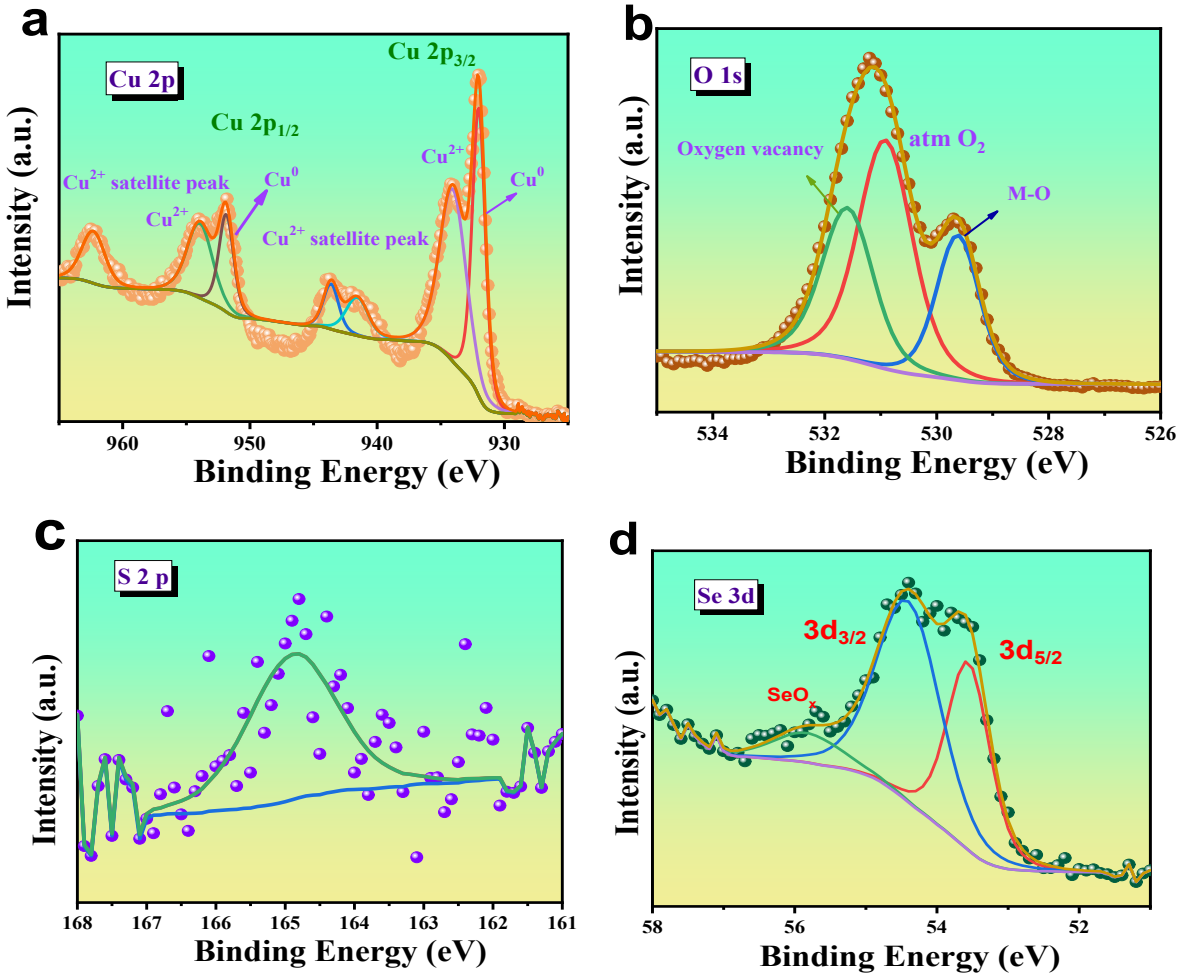


Figure S7. *XPS spectra of Cu_2S-Se-Hyd; high-resolution images of (a) Cu 2p; (b) O 1s; (c) S 2p and (d) Se 3d.*

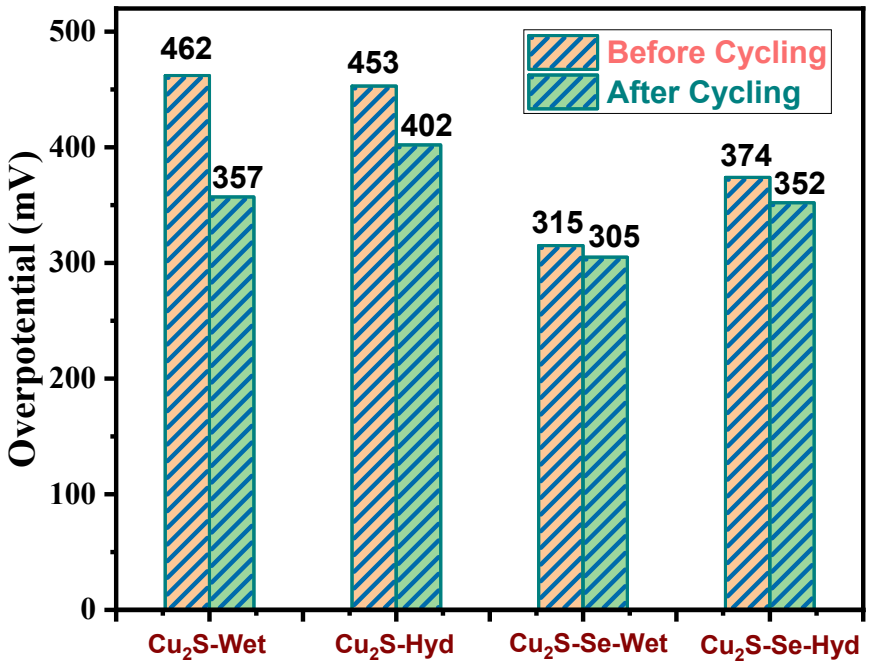


Figure S8. *Bar diagram for the overpotential comparison before and after cycling study.*

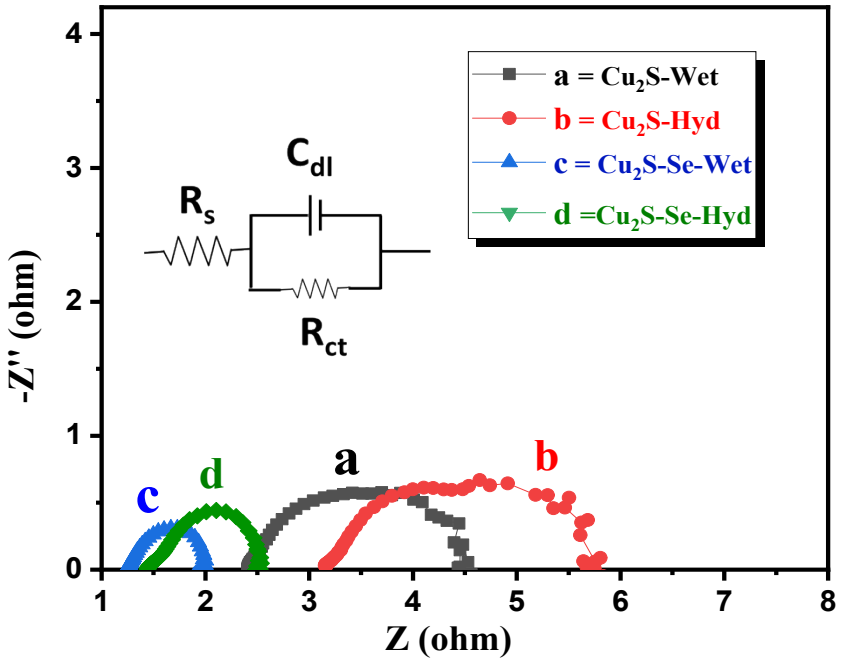


Figure S9. *Post EIS study for Cu_2S-Wet, Cu_2S-Hyd, Cu_2S-Se-Wet and Cu_2S-Se-Hyd.*

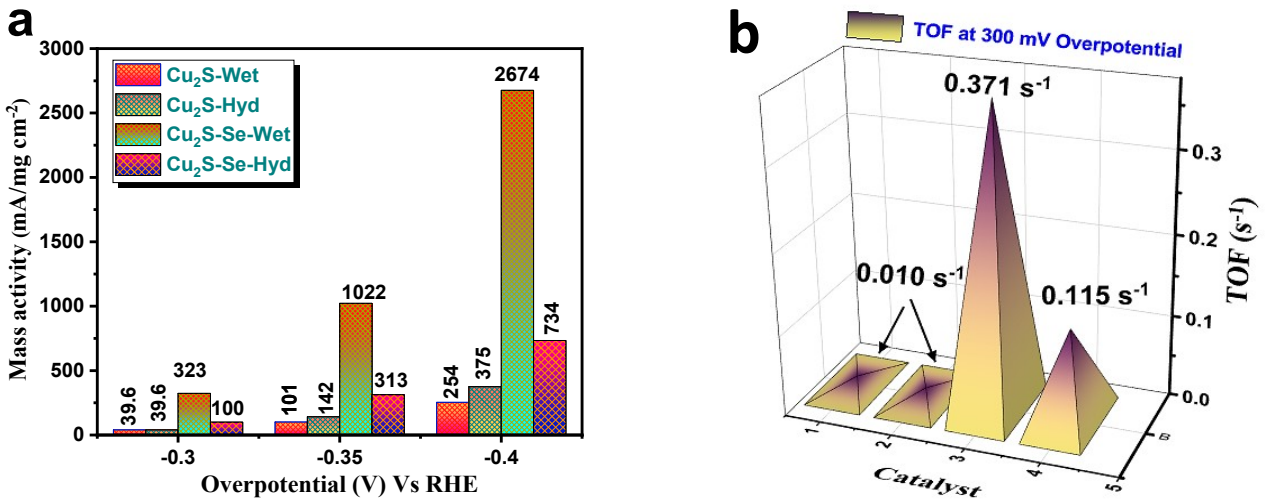


Figure S10. *(a) Mass activity calculated at different current density and (b) Turnover frequency (TOF) calculated at 300 mV overpotential.*

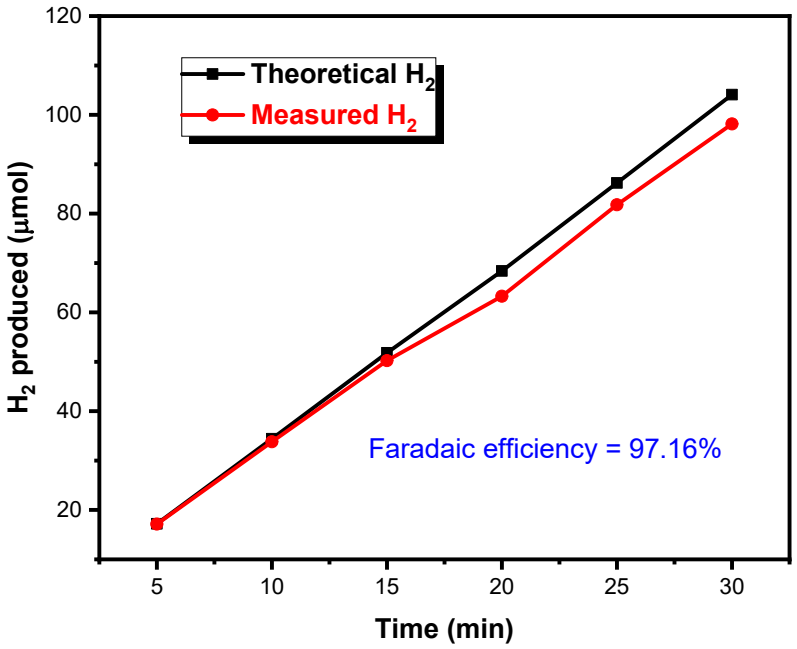


Figure S11. *Faradaic efficiency calculated for Cu_2S-Se-Wet and plot compared with theoretical calculation Vs time.*

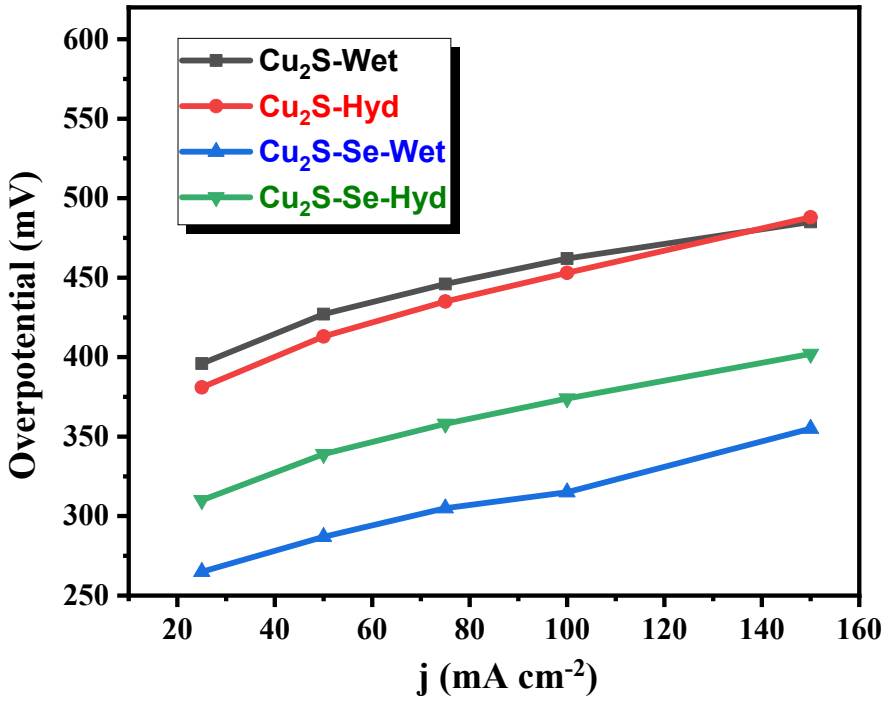


Figure S12. *The potential Vs current density plot for all the four catalyst.*

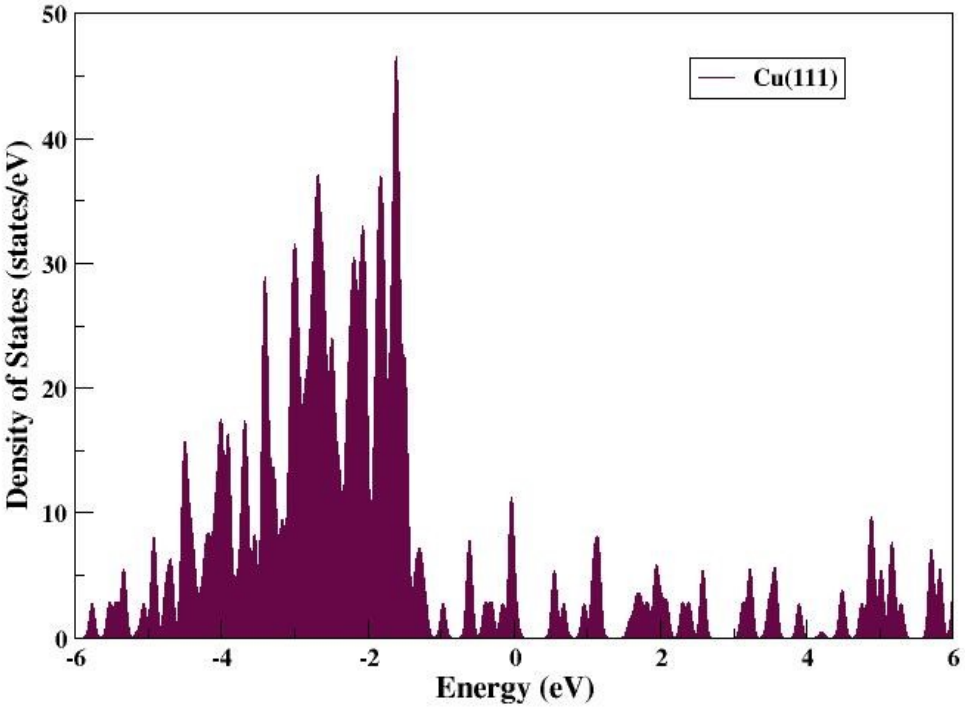


Figure S13. *Total pDOS of Cu(111) plane.*

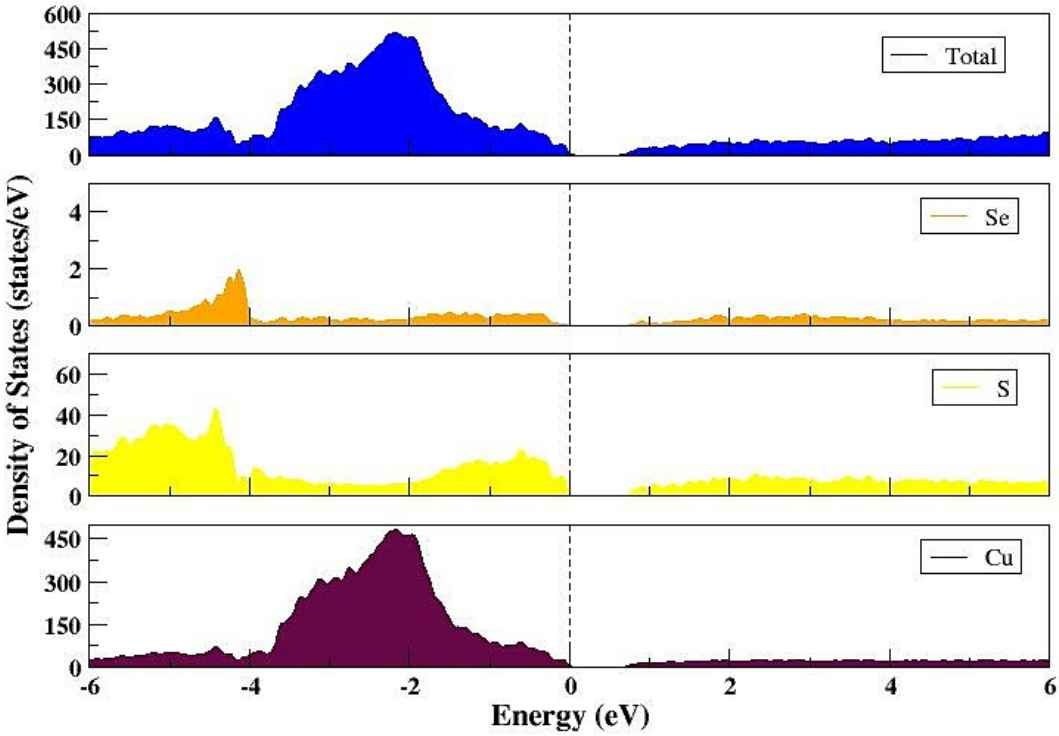


Figure S14. *Total pDOS of Cu_2S-Se system.*

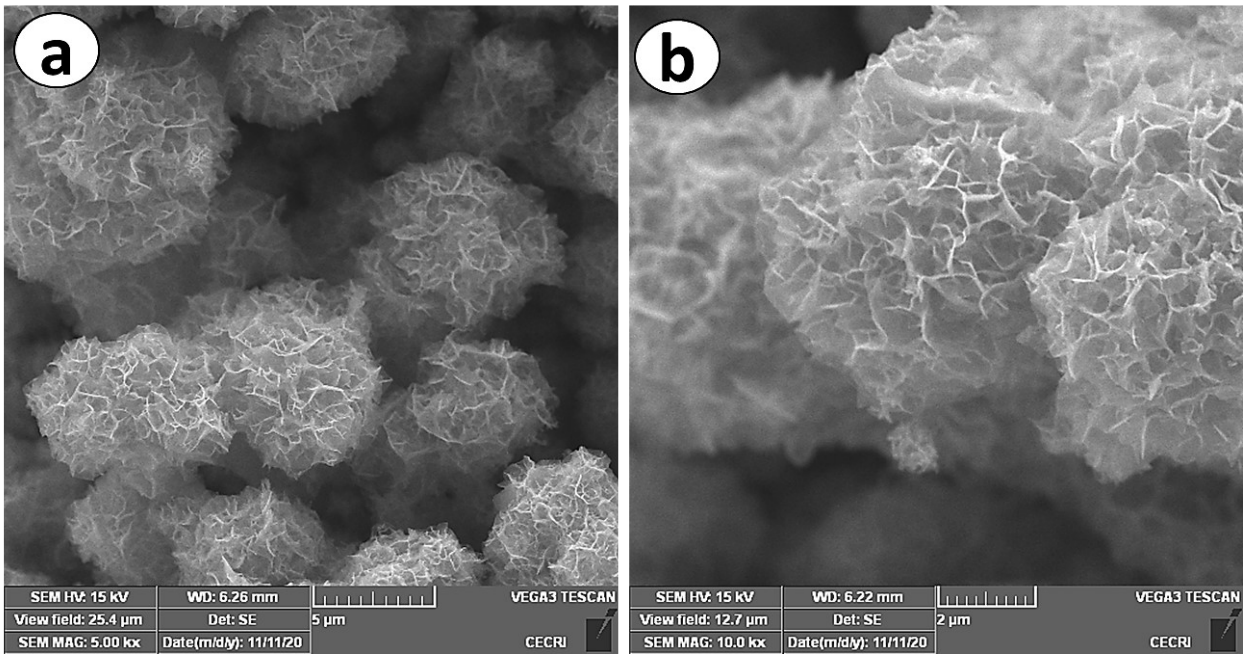


Figure S15. *Low and High magnified post SEM images of layered structure of Cu_2S-Se-Wet catalyst.*

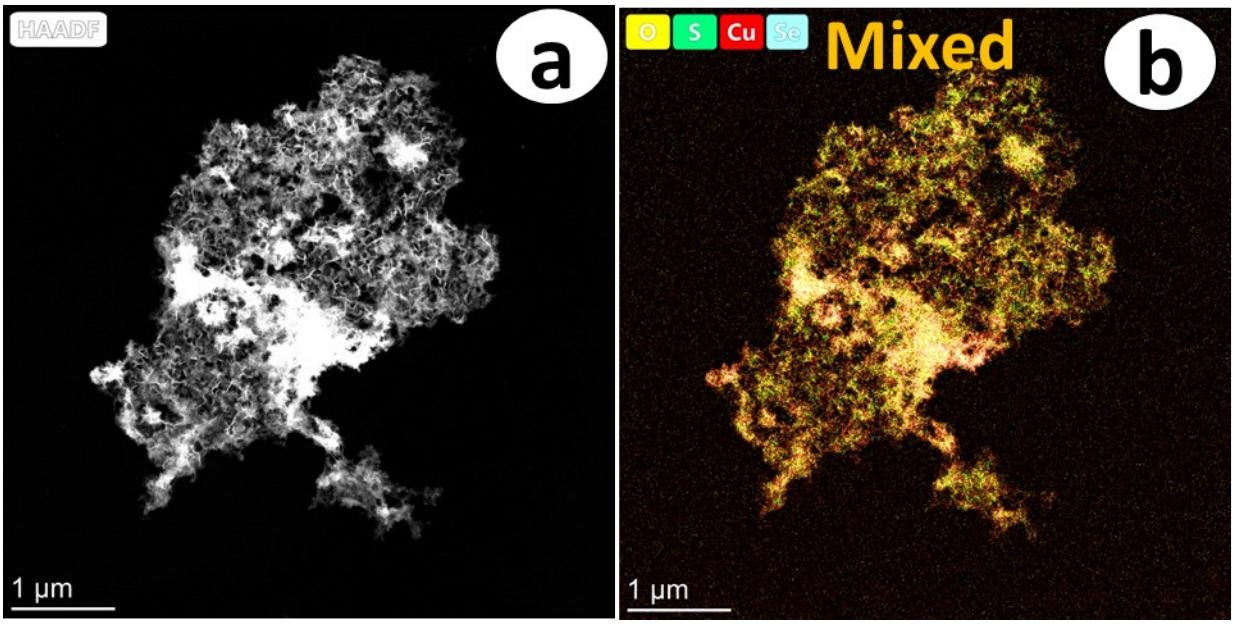


Figure S16. *(a) Post HR-TEM image of layered Cu_2S-Se-Wet. (b) mixed post HAADF elemental mapping of Cu_2S-Se-Wet.*

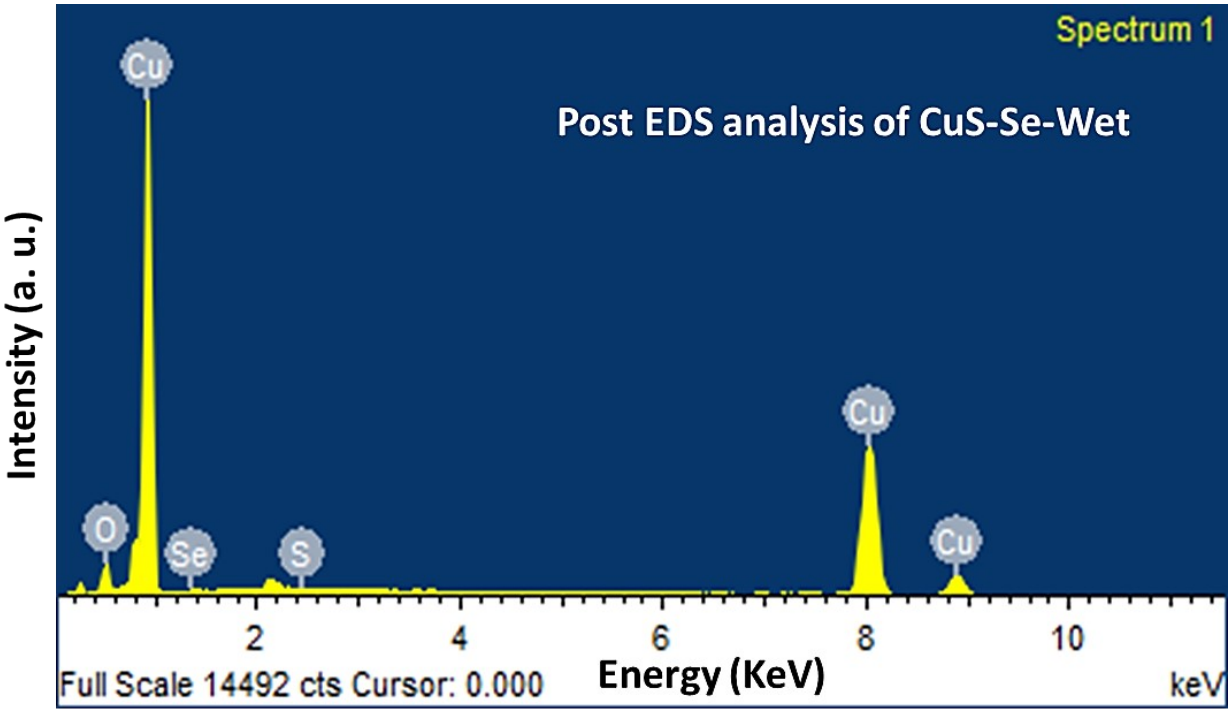


Figure S17. *Post EDS analysis of the wet-chemical sample Cu_2S-Se-Wet.*

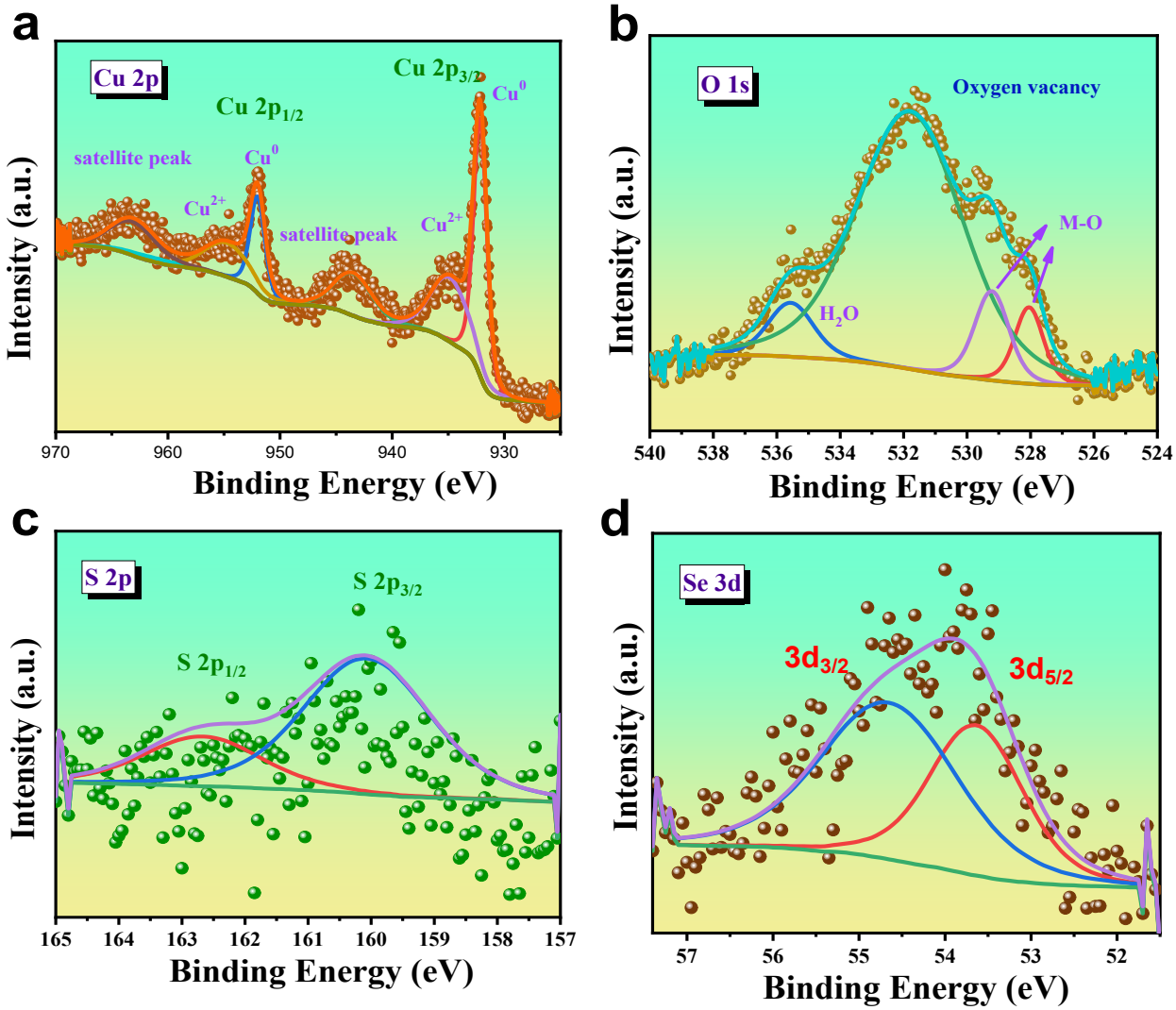


Figure S18. *Post XPS spectra of Cu_2S-Se-Wet; high-resolution images of (a) Cu 2p; (b) O 1s; (c) S 2p and (d) Se 3d.*

Table S1. Comparison of HER performance of Cu_2S-Se-Wet catalyst with other transition metal based catalyst in terms of methodology, overpotential, Tafel slope, binder and substrate.

Catalysts	Synthesis methods	Overpotential @ 10 mA cm^{-2}	Tafel (mV/dec)	Binder	Substrate	Reference
$NiCo_2S_4$	Hydrothermal	345 mV	60	Nafion	Glassy Carbon	1
Cu_2S	Hydrothermal	312 mV	49.79	Nafion	Graphite rod	2
NiS_x	Atomic layer deposition	440 mV	62	-	FTO	3
Ni–WSe_2	Wet chemical synthesis	259 mV	86	Nafion	Glassy Carbon	4
MoS_2 Nanosheet arrays	Physical vapour deposition	224 mV	58	-	Carbon Cloth	5
NiS_2/GS	Chemical growth	240 mV	41	-	Graphite	6
CoS_2	Hydrothermal	254 mV	90	Nafion	Glassy Carbon	7
$CoSe_2$	Hydrothermal	125 mV	45	-	Ti foil	8
α- NiS	Topotactic conversion	105 mV	40	-	Glassy Carbon	9
$NiSe_2$	Solvothermal	147 mV	63	NMP	Carbon paper	10
Cu_2S-Se-Wet	**Wet-chemical**	**230 mV**	**97**	**-**	**Cu Foam**	**This work**

References

1 U. Aftab, A. Tahira, R. Mazzaro, V. Morandi, M. Ishaq Abro, M. M. Baloch, C. Yu and Z. H. Ibupoto, *RSC Adv.*, 2020, **10**, 22196–22203.

2 K. S. Bhat and H. S. Nagaraja, *J. Sci. Adv. Mater. Devices*, 2020, **5**, 361–367.

3 Y. Çimen, A. W. Peters, J. R. Avila, W. L. Hoffeditz, S. Goswami, O. K. Farha and J. T. Hupp, *Langmuir*, 2016, **32**, 12005–12012.

4 S. R. Kadam, A. N. Enyashin, L. Houben, R. Bar-Ziv and M. Bar-Sadan, *J. Mater. Chem. A*, 2020, **8**, 1403–1416.

5 X. Zhang, Y. Zhang, B. Bin Yu, X. L. Yin, W. J. Jiang, Y. Jiang, J. S. Hu and L. J. Wan, *J. Mater. Chem. A*, 2015, **3**, 19277–19281.

6 X. Wu, B. Yang, Z. Li, L. Lei and X. Zhang, *RSC Adv.*, 2015, **5**, 32976–32982.

7 R. A. Senthil, J. Pan, Y. Wang, S. Osman, T. R. Kumar and Y. Sun, *Ionics (Kiel).*, 2020, **26**, 6265–6275.

8 C. P. Lee, W. F. Chen, T. Billo, Y. G. Lin, F. Y. Fu, S. Samireddi, C. H. Lee, J. S. Hwang, K. H. Chen and L. C. Chen, *J. Mater. Chem. A*, 2016, **4**, 4553–4561.

9 X. Long, G. Li, Z. Wang, H. Zhu, T. Zhang, S. Xiao, W. Guo and S. Yang, *J. Am. Chem. Soc.*, 2015, **137**, 11900–11903.

10 Z. Li, X. Ma, L. Wu, H. Ye, L. Li, S. Lin, X. Zhang, Z. Shao, Y. Yang and H. Gao, *RSC Adv.*, 2021, **11**, 6842–6849.