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Supporting information

Copper dopants improved hydrogen evolution activity of earth-abundant cobalt pyrite catalysts by activating the electrocatalysis inert sulfur sites

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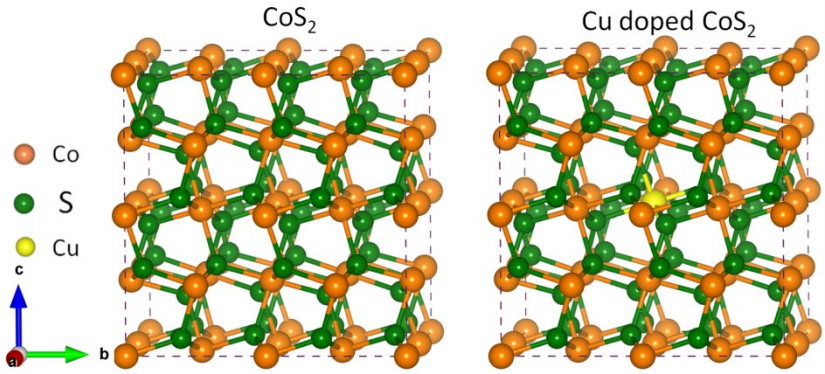


Figure S1. Optimized atomic structures of CoS_2 and Cu doped CoS_2 (2×2×2 supercell).

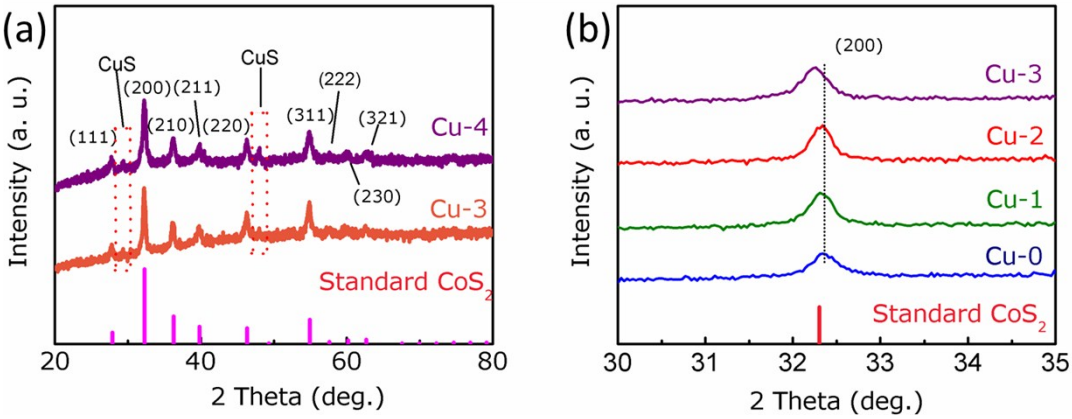


Figure S2. (a) XRD results of sample Cu-3 and Cu-4, where the CuS phase appears gradually.(b) XRD results of sample Cu-0, Cu-1, Cu-2 and Cu-3 ranging from 30^0 to 35^0.

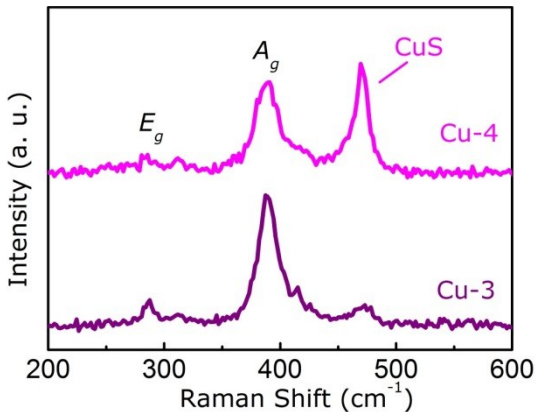


Figure S3. Raman results of sample Cu-3 and Cu-4.

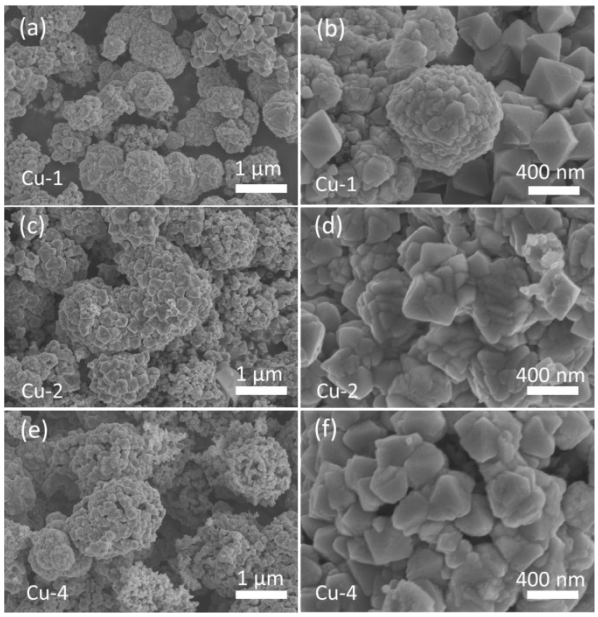


Figure S4. Scanning electron microscope (SEM) images of (a), (b) Cu-1. (c), (d) Cu-3 and (e), (f) Cu-4.

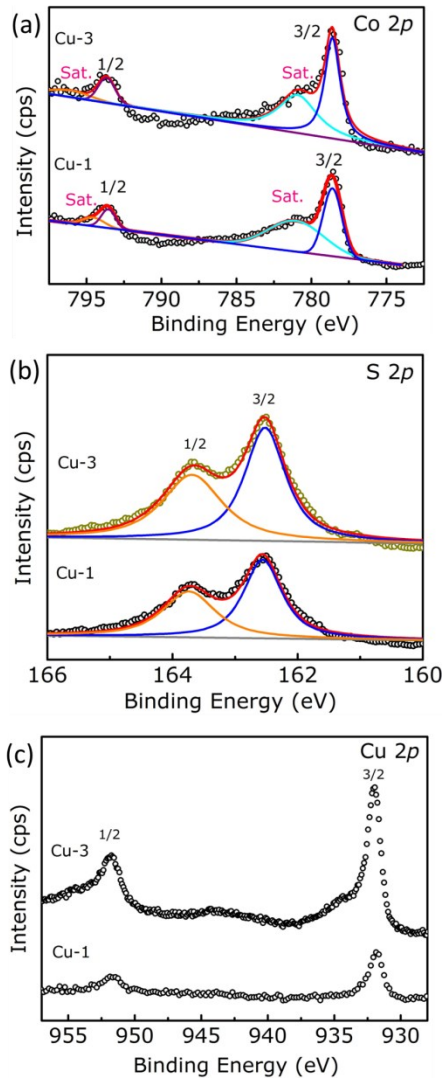


Figure S5. X-ray photoelectron spectra (XPS) results of Cu-1 and Cu-3 : (a) Co 2p, (b) S 2p and (c) Cu 2p regions.

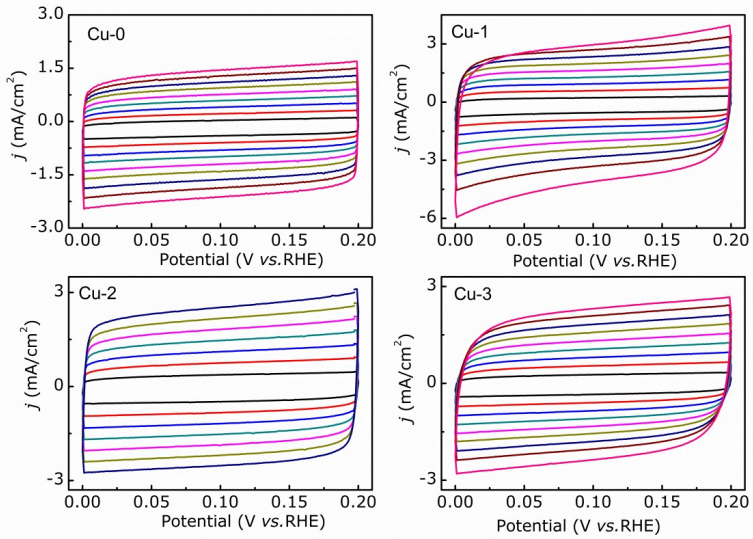


Figure S6. Cyclic voltammetry curves of sample Cu-0, Cu-1, Cu-2 and Cu3 in the region of 0 – 0.2 V *vs.* RHE.

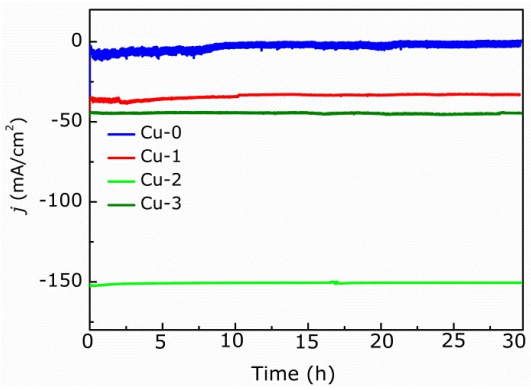


Figure S7. The time-dependent current density as a function of time at a static overpotential of 200 mV without iR correction for sample Cu-0, Cu-1, Cu-2 and Cu3.

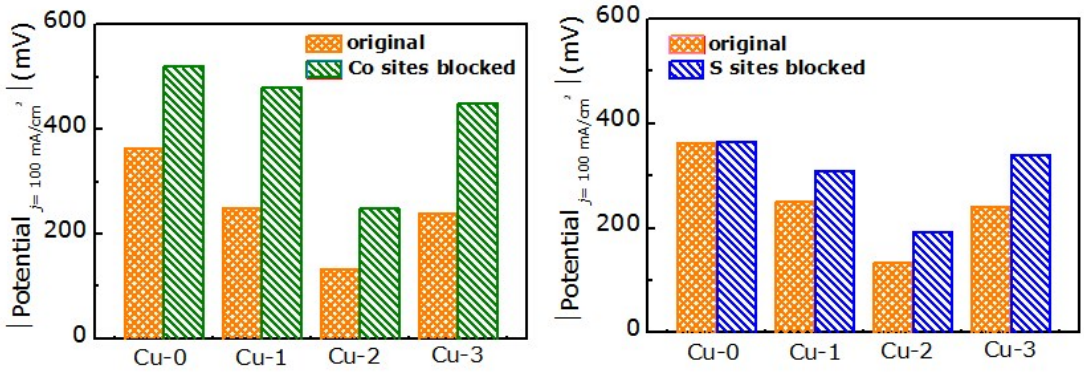
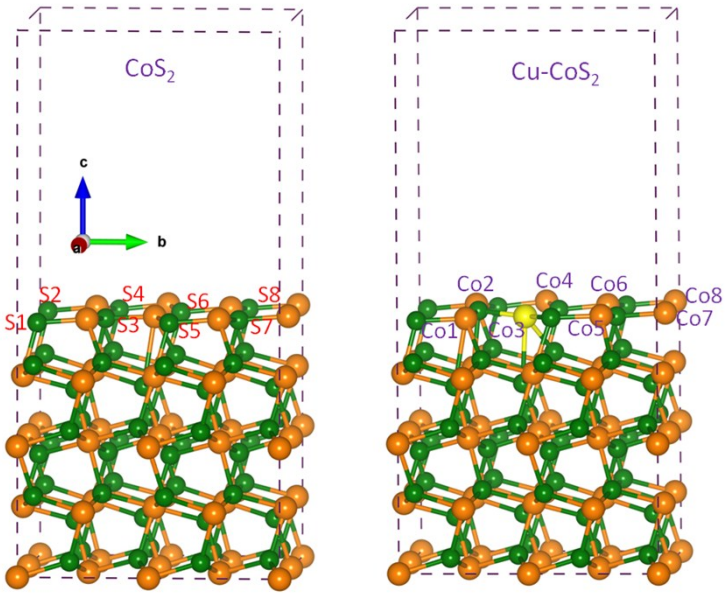
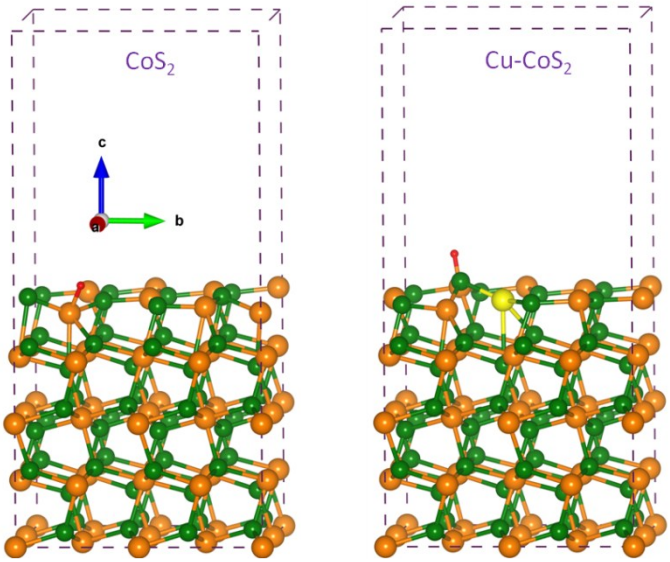


Figure S8. The overpotentials of sample Cu-0, Cu-1, Cu-2 and Cu3 at current density of 100 mV before and after blocking their Co sites and S sites, respectively.



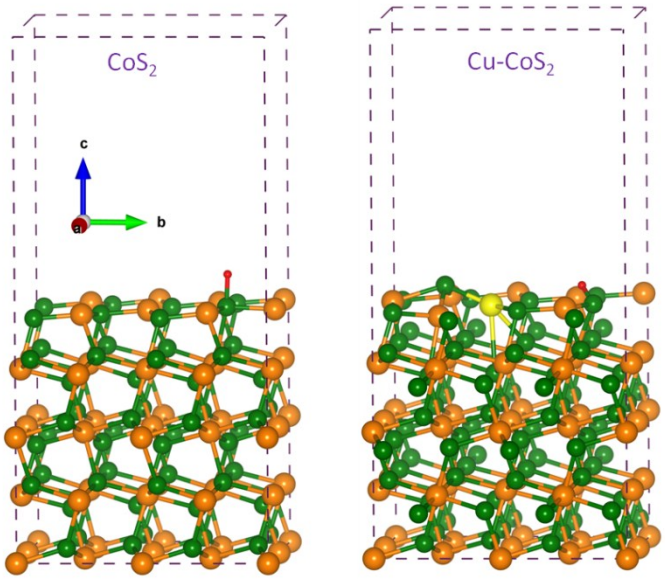
site	CoS_2	Cu-CoS_2	site	CoS_2	Cu-CoS_2
S1	6.442	6.480	Co1	8.555	8.536
S2	6.487	6.462	Co2	8.530	8.523
S3	6.511	6.671	Co3(Cu)	8.518	10.535
S4	6.455	6.444	Co4	8.510	8.496
S5	6.490	6.493	Co5	8.511	8.552
S6	6.440	6.447	Co6	8.529	8.514
S7	6.466	6.454	Co7	8.514	8.490
S8	6.443	6.441	Co8	8.544	8.451

Figure S9. optimized atomic structure of CoS_2 and Cu doped CoS_2 surface with their calculated bader charge for the surface atoms.



site	CoS_2	Cu-CoS_2	site	CoS_2	Cu-CoS_2
S1	6.420	6.329	Co1	8.558	8.826
S2	6.489	6.143	Co2	8.538	9.118
S3	6.429	6.176	Co3(Cu)	8.511	10.847
S4	6.449	6.351	Co4	8.507	8.508
S5	6.435	6.218	Co5	8.541	8.841
S6	6.443	6.462	Co6	8.527	8.835
S7	6.468	6.443	Co7	8.507	8.736
S8	6.442	6.198	Co8	8.535	9.051
-	-	-	H	1.128	0.942

Figure S10. Optimized atomic structure of CoS_2 and Cu doped CoS_2 surface with H atom absorption on Co site and their calculated bader charge for the surface atoms.



site	CoS_2	Cu-CoS_2	site	CoS_2	Cu-CoS_2
S1	6.446	6.259	Co1	8.551	8.596
S2	6.490	6.485	Co2	8.532	8.485
S3	6.456	6.454	Co3(Cu)	8.556	10.571
S4	6.459	6.456	Co4	8.513	8.501
S5	6.452	6.533	Co5	8.554	8.498
S6	6.449	6.455	Co6	8.541	8.538
S7	5.504	6.630	Co7	8.524	8.491
S8	6.440	6.455	Co8	8.546	8.542
H	1.877	0.901	-	–	-

Figure S11. Optimized atomic structure of CoS_2 and Cu doped CoS_2 surface with H atom absorption on S site and their calculated bader charge for the surface atoms.

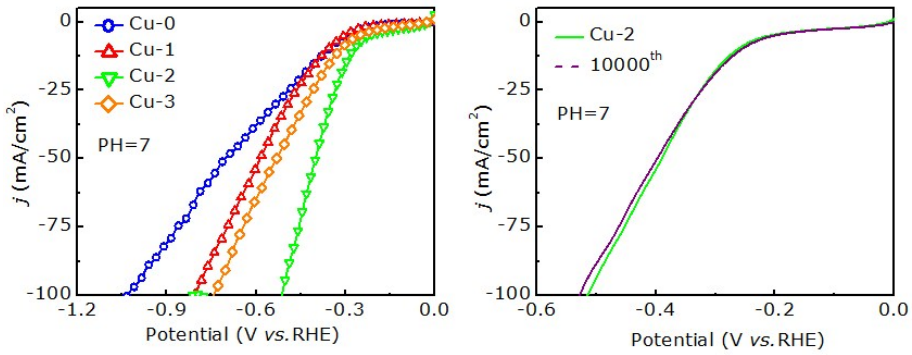


Figure S12. Polarization curves recorded for Cu doped CoS_2 catalysts in 1.0 M PBS .

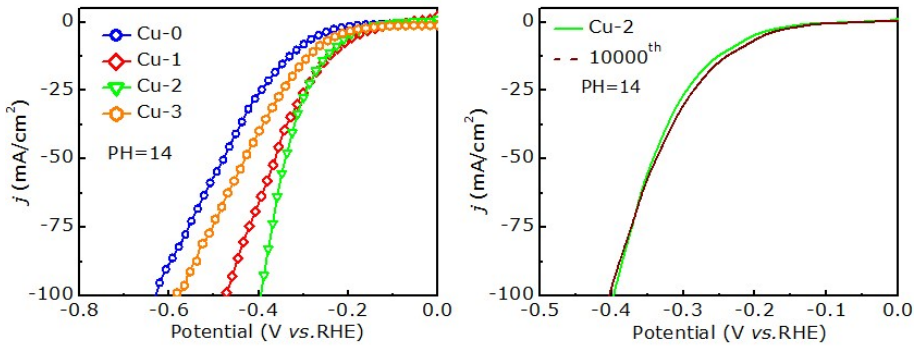


Figure S13. Polarization curves recorded for Cu doped CoS_2 catalysts in 1.0 M KOH.

Table S1. Comparison of electrocatalysts for HER in 0.5 M H_2SO_4.

Catalyst	Onset potential [V *vs.*RHE]	η at $J = 10$ mA/cm^2 [mV]	η at $J = 100$ mA/cm^2 [mV]	Tafel slope (mV/dec)	Exchange current density (mA/cm^2)	Reference No.
Cu-2	20	52	133	42	0.68	This work
CoS_2	101	192	-	52	3.53×10^{-3}	1
$(Fe_{0.48}Co_{0.52})S_2$	125	196	-	47.5	0.959×10^{-3}	1
$(Co_{0.59}Ni_{0.41})S_2$	148	-	-	50.4	0.0476×10^{-3}	1
$CoSe_2$(300℃)	70	149	171	31.2	-	2
MoS_2/CoS_2/CC	-	87	261	73.4	-	3
CoS_2-MoS_2	70	185	-	67.96	-	4
$CoS_{2x}Se_{2(1-X)}$	102	129.5	174	44	-	5
CoS_2@WS_2/CC	-	97.2	164	66	-	6
$Ni_{2.3\%}$-CoS_2/CC	-	181	240	106	-	7
Zn-Co-S/TM	-	188	382	164	-	8
CoS_2 NPA	61	70	140	64.5	-	9
CoS_2/P	25	67	118	50	0.47	10
CoPS NWs	-	61	-	48	0.554	11
CoS/P/CNT	-	48	109	55	1.14	12
CoS2/RGO-5 %	-	143	346	285	-	13

Reference

1. M. S. Faber, M. A. Lukowski, Q. Ding, N. S. Kaiser, S. Jin, *J. Phys. Chem. C*, 2014, **118**, 21347-21356.
2. H. Zhang, B. Yang, X. Wu, Z. Li, L. Lei, X. Zhang, *ACS Appl. Mater. Intersfaces*, 2015, **7**, 1772-1779.
3. J. Huang, D. Hou, Y. Zhou, W. Zhou, G. Li, Z. Tang, S. Chen, *J. Mater. Chem. A*, 2015, **3**, 22886-22891.
4. J. Huang, D.Hou, Y. Zhou, W. Zhou, G. Li, Z. Tang, S. Chen, *J. Mater. Chem. A*, 2015, **3**, 22886-22891.
5. K. Liu, F. Wang, K. Xu, T. A. Shifa, Z. Cheng, X. Zhan, J. He, *Nanoscale*, 2016, **8**, 4699-4704.
6. X. Zhou, X. Yang, H. Li, M. N. Hedhili, K. W. Huang, L. J. Li, W. Zhang, *J. Mater. Chem. A*, 2017.
7. W. Fang, D. Liu, Q. Lu, X. Sun, A. M. Asiri, *Electrochem. Commun.*, 2016, **63**, 60-64.
8. Y. Liang, Q. Liu, Y. Luo, X. Sun, Y. He, A. M. Asiri, *Electrochim. Acta*, 2016, **190**, 360-364.
9. H. Zhang, Y. Li, G.Zhang, T. Xu, P. Wan, X. Sun, *J. Mater. Chem. A*, 2015, **3**, 6306-6310.
10. C. Ouyang, X. Wang, S. Wang, *Chem. Commun*., 2015, **51**, 14160-14163.
11. M. Cabán-Acevedo, M. L. Stone, J. R. Schmidt, J. G. Thomas, Q. Ding, H. C. Chang, S. Jin, *Nat. Mater.*, 2015, **14**, 1245-1251.
12. W. Liu, E. Hu, H. Jiang, Y. Xiang, Z. Weng, M. Li, H. Wang, *Nat. Commun.*, 2016, **7**.
13. W. Xing, Y. Zhang, Q. Xue, Z. Yan, *Nanoscale Res. Lett.*, 2015, **10**, 488.