

Supporting Information

In-Situ Generated Cu-Co-Zn Trimetallic Sulfides Nanoflowers on Copper Foam: a Highly Efficient OER Electrocatalyst

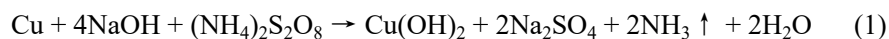
Jie Bai, Nana Lei, Limin Wang*, Yaqiong Gong*

School of Chemical Engineering and Technology, North University of China, Taiyuan,
030051, P. R. China

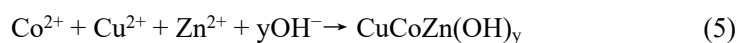
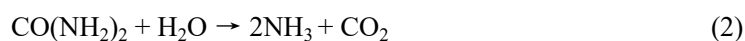
* Email: wanglimin@nuc.edu.cn (Limin Wang); gyq@nuc.edu.cn (Yaqiong Gong)

Some descriptions of the principles and the reaction process as follows. Eqs. (1)-(9).

Pretreated copper hydroxide was grown on CF:



The precipitation and infusion of multiple cations lead to an increment in the extent of redox reactions. Adding urea served as a constant source of CO_3^{2-} and OH^- ions, which on reaction with precursor metal ions, stabilized the formation of hydroxides. The presence of NH_4F is beneficial to maintain the needle-like morphology:



When Na_2S is added, metal ions react with sulfur ions and the reaction process is roughly as follows:

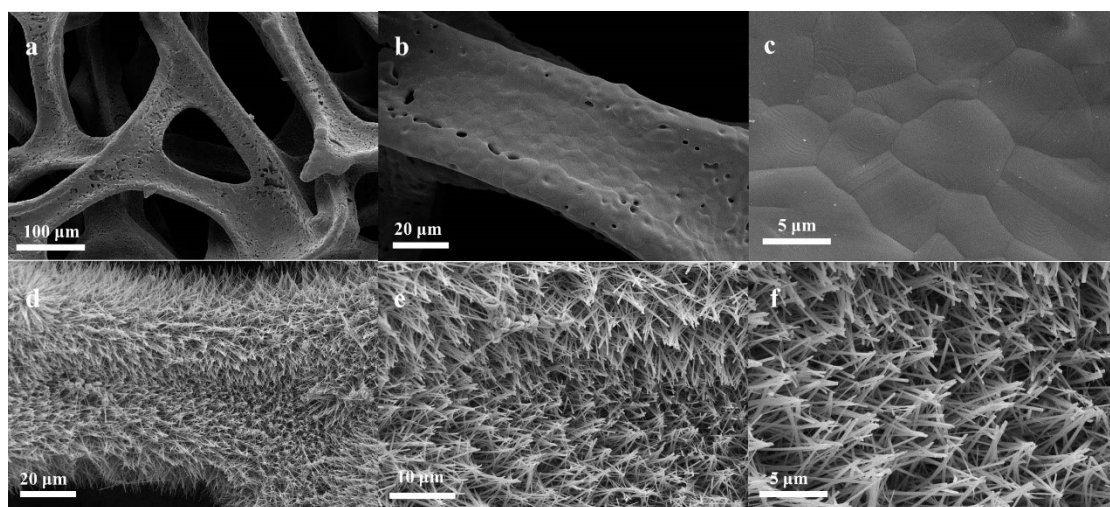


Fig. S1. SEM images of (a-c) Cu foam at high and low magnifications and images of (d-f) $\text{Cu}(\text{OH})_2$.

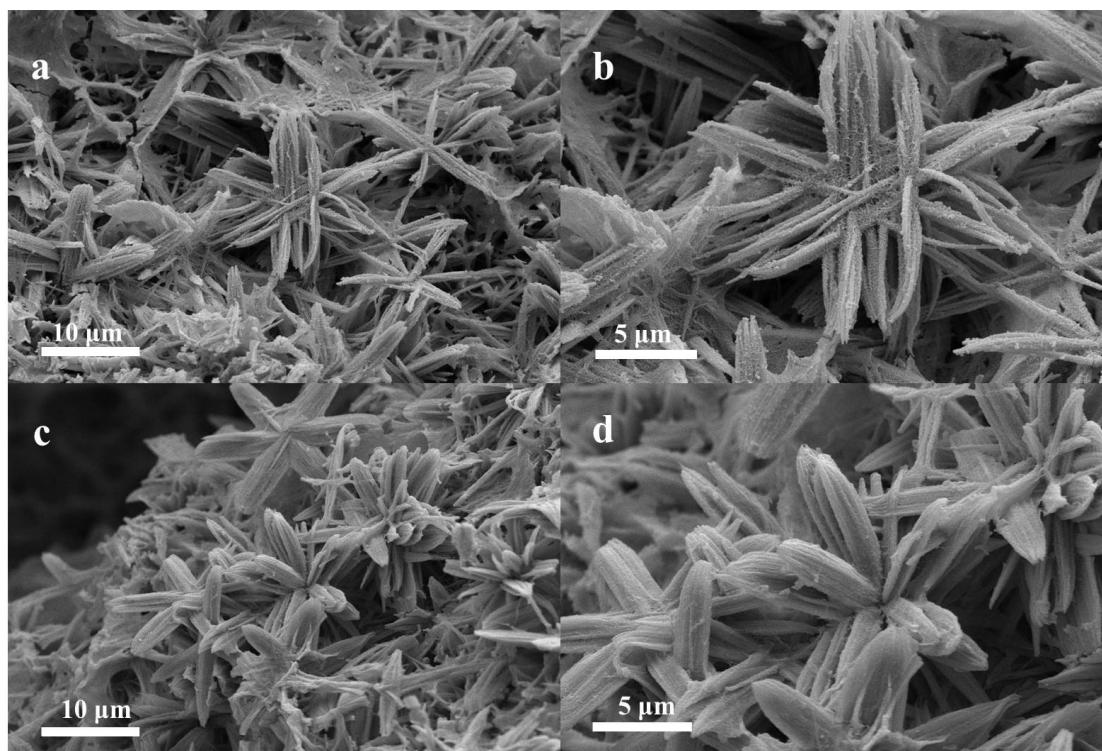


Fig. S2. SEM images of (a,b) CuCoZn-S-1 and (c,d) CuCoZn-S-6.

Table S1. Elemental composition of Cu, Co and Zn determined by ICP-OES.

Element	Cu	Co	Zn
Content (Wt %)	90.16	6.10	3.20

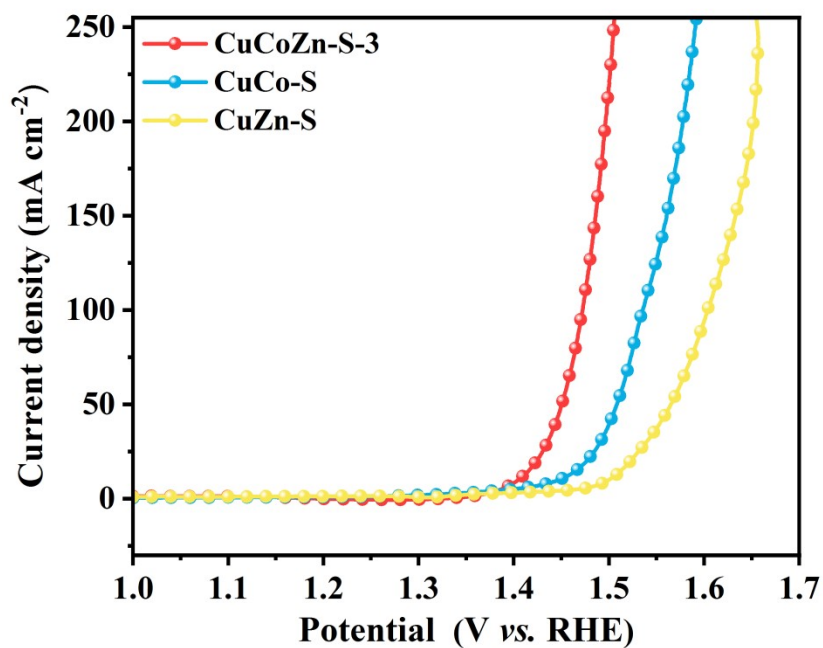


Fig. S3. LSV curves of CuCoZn, CuCo-S and CuZn-S cured for 3 h.

Table S2. The comparison of OER catalytic performances between CuCoZn-S-3 and other materials recently reported in the literatures.

Catalyst	Overpotential (mV)	Tafel slope (mV dec ⁻¹)	Electrolyte	Reference
CuCoZn-S-3	175@10	62.3	1.0M KOH	This work
MoNiFeS_x@FeNi₃	192@10	72.8	1.0M KOH	1
NiFeCoS_x@FeNi₃	210@10	45	1.0M KOH	2
Fe-Ni₃S₂@FeNi₃-8	213@10	83	1.0M KOH	3
(Ni,Fe)S₂/MoS₂	270@10	43.21	1.0M KOH	4
Ni-Co-S-P	280@10	69	1.0M KOH	5
FeNi/(FeNi)₉S₈	283@10	95.1	1.0M KOH	6
MoS₂/NiCoS	290@10	77	1.0M KOH	7

Table S3. The comparison of OER catalytic performances of other trimetallic oxides and phosphide materials recently reported in the literatures.

Electrocatalysts	Overpotential (mV)	Tafel slope (mV dec ⁻¹)	Electrolyte	Reference
In ₂ O ₃ /ZnO/Co ₃ O ₄	398	88	1.0 M KOH	8
Cu _x Mo _x /Co _{1-x} O NPs@RGO	250	61	1.0 M KOH	9
Co ₃ Fe ₄ V ₃ O _x	249	41	1.0 M KOH	10
CoFeNi-O-1	244	55.4	1.0 M KOH	11
NiFeCoP@CAP/NF,	202	28.9	1.0 M KOH	12
CoNiFeP	261	49.5	1.0 M KOH	13
np-NiFeCoP	244	41.4	1.0 M KOH	14
NiCoFe-P-NP@NiCoFe- PBA	223	78	1.0 M KOH	15

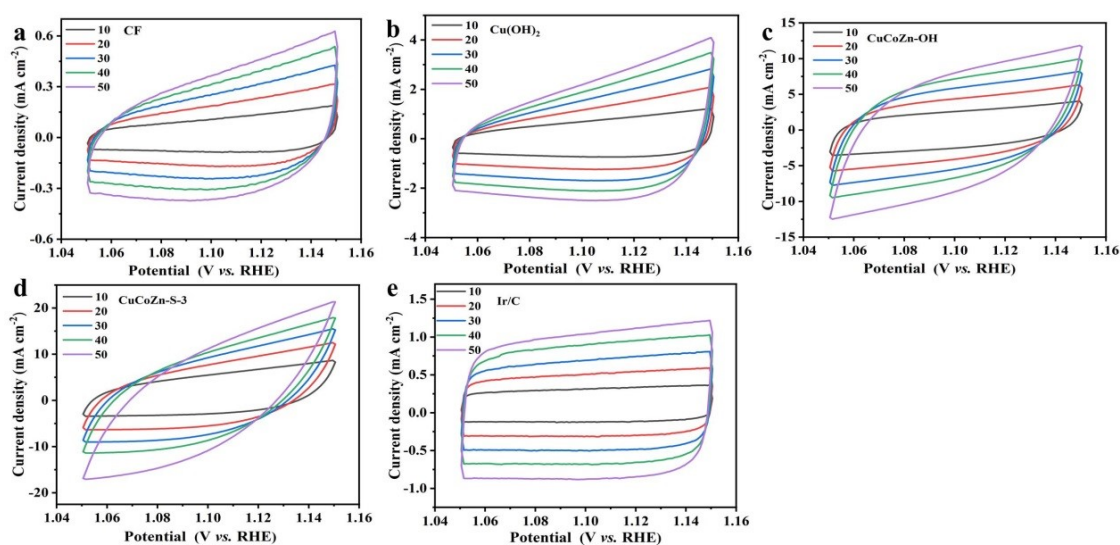


Fig. S4. Cyclic voltammograms at different scan rates (10, 20, 30, 40 and 50 mV S⁻¹). (a) CF, (b) Cu(OH)₂, and (c) CuCoZn-OH, (d) CuCoZn-S-3 and (e) Ir/C.

Table S4. Comparison of OER activity of CuCoZn-S catalysts with different time at 1 M KOH.

Catalysts	η_{10} (mV)	η_{100} (mV)
CuCoZn-S-1	180	262
CuCoZn-S-6	188	286

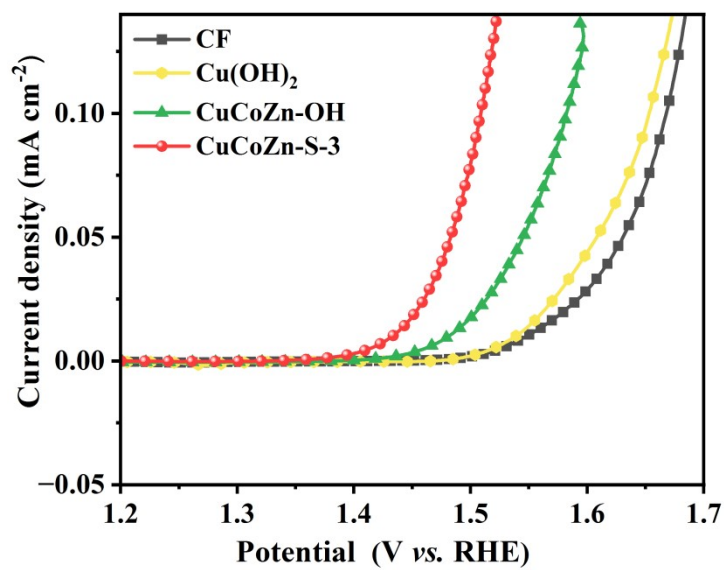


Fig. S5. ECSA-normalized LSV curves of CF, Cu(OH)₂, CuCoZn-OH and CuCoZn-S-3.

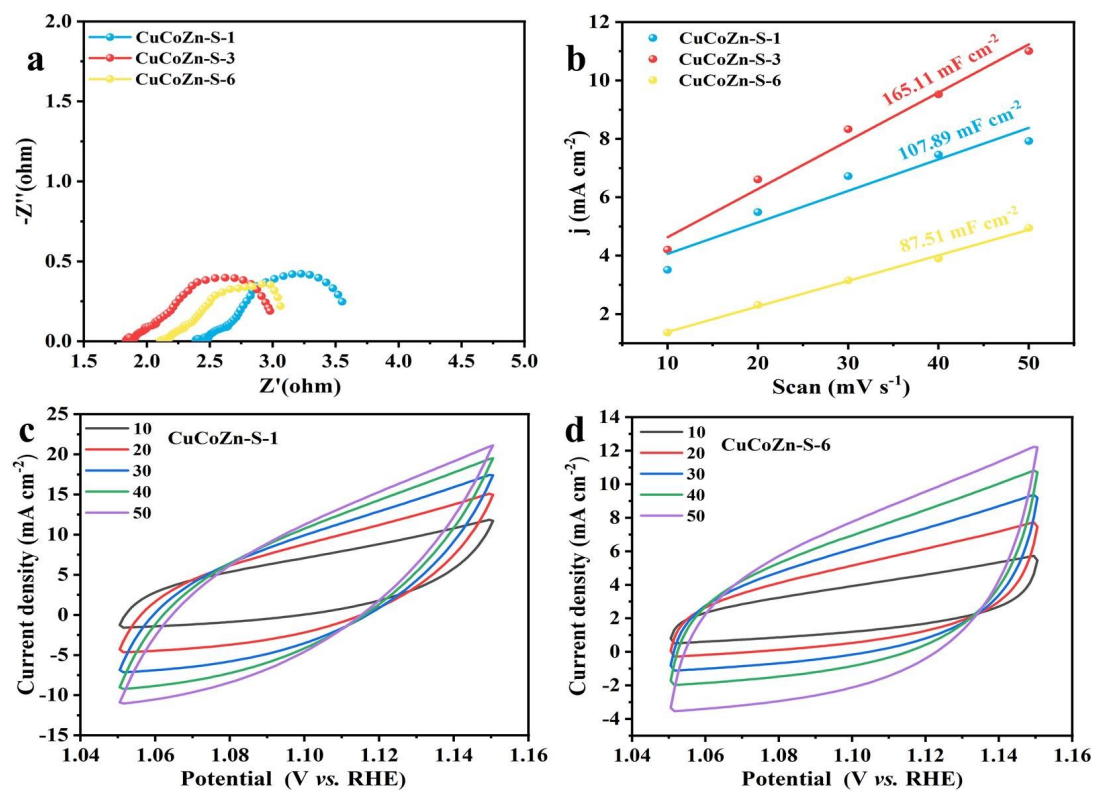


Fig. S6. Comparison image of different curing time. (a) Nyquist plots. (b) corresponding C_{dl} values. (c) Cyclic voltammograms of CuCoZn-S-1 and (d) Cyclic voltammograms of CuCoZn-S-6.

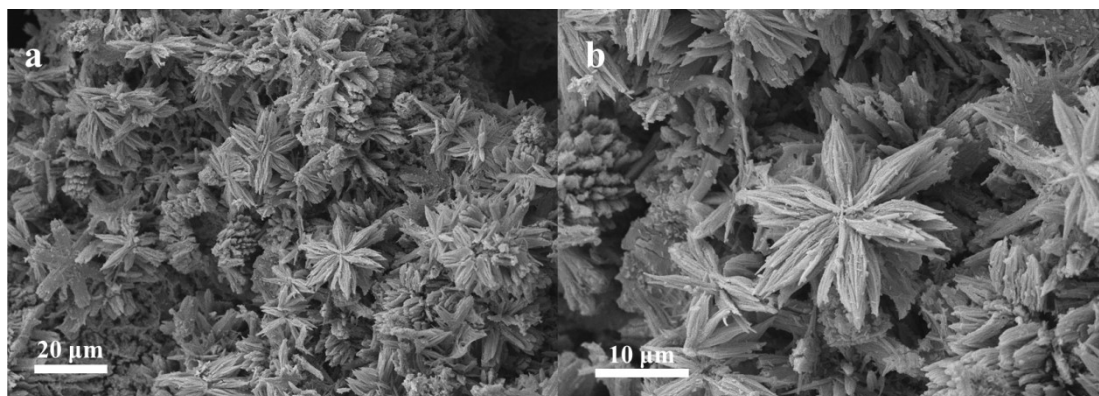


Fig. S7. SEM image of OER stability test.

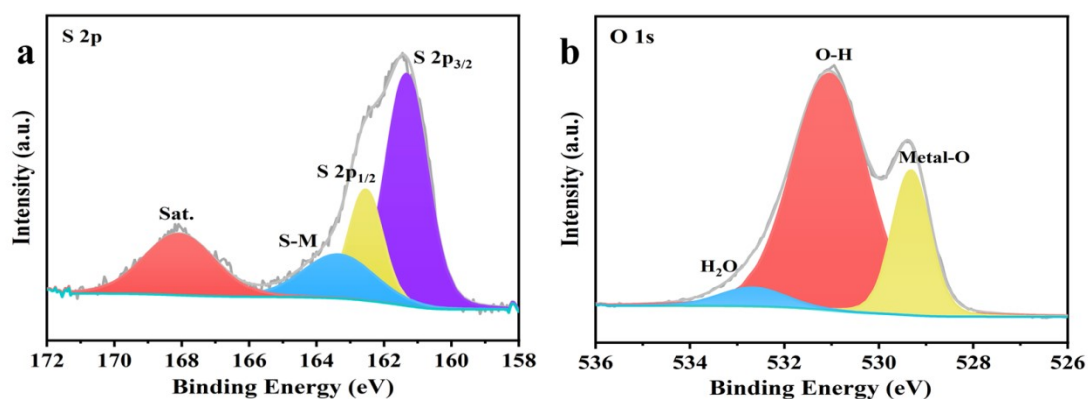


Fig. S8. XPS spectrum after OER stability test. (a) S 2p and (b) O 1s.

References

- 1 Q. Li, W. Zhang, J. Shen, X. Zhang, Z. Liu, J. Liu, J. Alloys Compd., 2022, **902**, 163670.
- 2 J. Shen, Q. Li, W. Zhang, Z. Cai, L. Cui, X. Liu, J. Liu, J. Mater. Chem. A, 2022, **10**, 5442-5451.
- 3 W. Zhang, Q. Jia, H. Liang, L. Cui, D. Wei, J. Liu, Chem. Eng. J., 2020, **396**, 125315.
- 4 Y. Liu, S. Jiang, S. Li, L. Zhou, Z. Li, J. Li, M. Shao, Appl. Catal. B Environ., 2019, **247**, 107-114.
- 5 Y. Tian, Z. Lin, J. Yu, S. Zhao, Q. Liu, J. Liu, R. Chen, Y. Qi, H. Zhang, R. Li, J. Li, J. Wang, ACS Sustain. Chem. Eng., 2019, **7**, 14639-14646.
- 6 H. Meng, S. Lin, J. Feng, L. Zhang, A. Wang, J. Colloid Interface Sci., 2022, **610**, 573-582.
- 7 C. Qin, A. Fan, X. Zhang, S. Wang, X. Yuan, X. Dai, J. Mater. Chem. A, 2019, **7**, 27594-27602.
- 8 P. Ilanchezhian, G. M. Kumar, C. Siva, A. Madhankumar, H. C. Jeon, T. W. Kang and D. Y. Kim, Int. J. Hydrogen Energy, 2019, **44**, 23081-23090.
- 9 T. Niyitanga and H. Kim, Chem. Eng. J., 2023, **451**, 138649.
- 10 Chen, H. Li, Z. Pei, Q. Huang, Z. Yuan, C. Wang, X. Liao, G. Henkelman, Y. Chen and L. Wei, J. Mater. Chem. A, 2020, **8**, 15951-15961.
- 11 Z. Cao, Z. Jiang, Y. Li, C. Huang and Y. Li, ChemSusChem, 2019, **12**, 2480-2486.
- 12 S. Zhao, Y. Zhao, J. Chen, R. Dai, W. Zhou, J. Yang, X. Zhao, Z. Chen, Y. Zhou, H. Zhang and A. Chen, Electrochim. Acta, 2022, **426**, 140788.
- 13 Y. Zhang, Z. Li, K. Zhang, Z. Wu, F. Gao and Y. Du, Appl. Surf. Sci., 2022, **590**, 153102.
- 14 Y. Pang, W. Xu, S. Zhu, Z. Cui, Y. Liang, Z. Li, S. Wu, C. Chang and S. Luo, J. Mater. Sci. Technol., 2021, **82**, 96-104.
- 15 G. Zhang, Y. Li, X. Xiao, Y. Shan, Y. Bai, H. G. Xue, H. Pang, Z. Tian and Q. Xu, Nano Lett, 2021, **21**, 3016-3025.