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ZIF-67 derived $CuCo_2S_4$@CoS_2 as an efficient bifunctional electrocatalyst for Overall Water Splitting

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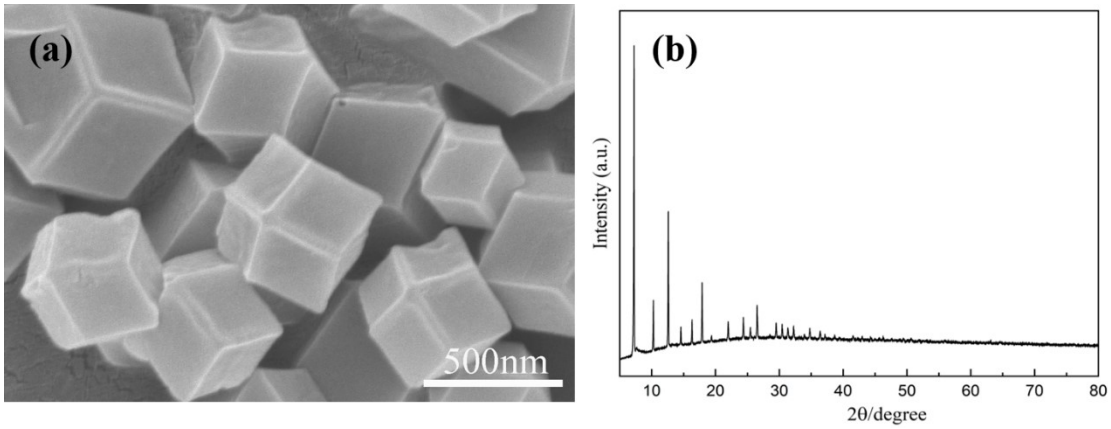

Fig S1. SEM and XRD results of the ZIF-67 template

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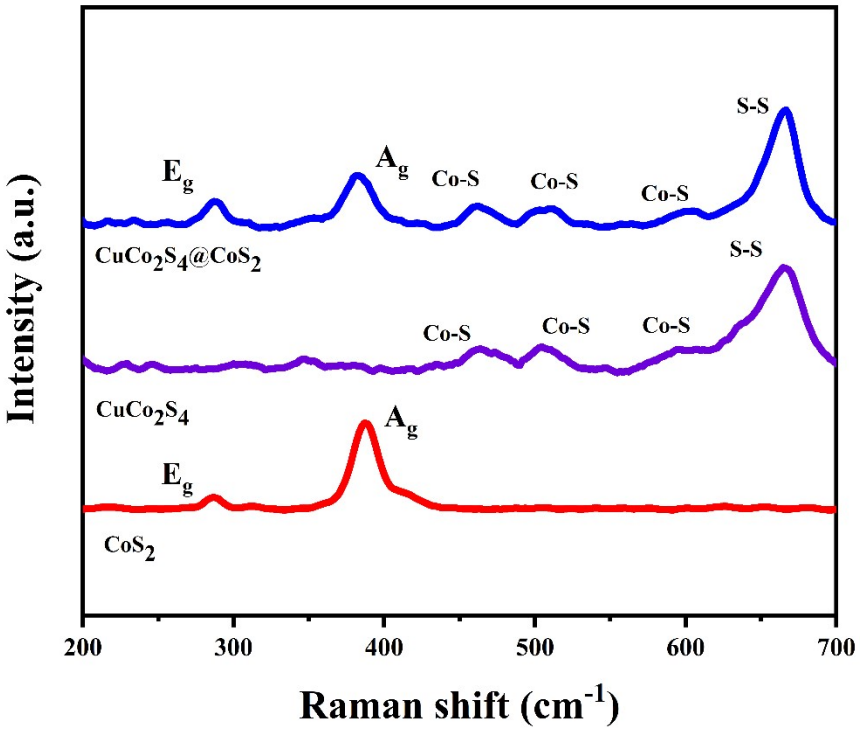

Fig S2. Raman spectra of CoS_2, $CuCo_2S_4$, and $CuCo_2S_4$@CoS_2.

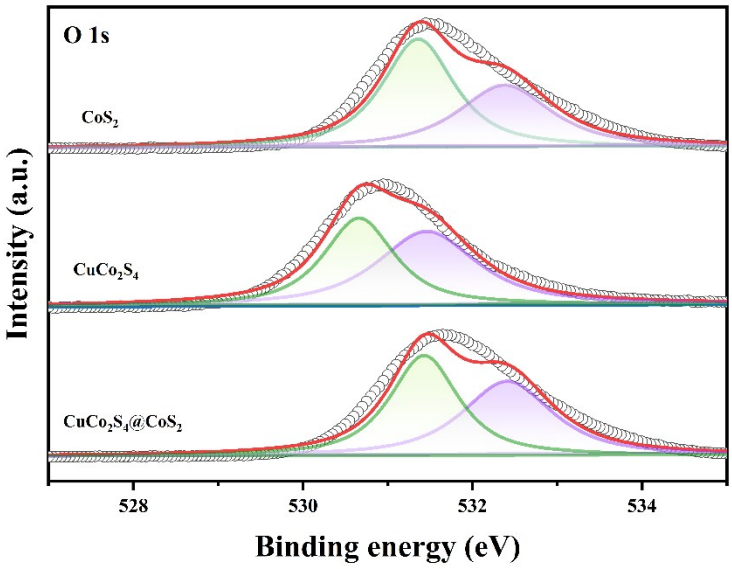

Fig S3. The O 1s XPS spectra of CoS_2, $CuCo_2S_4$, and $CuCo_2S_4$@CoS_2.

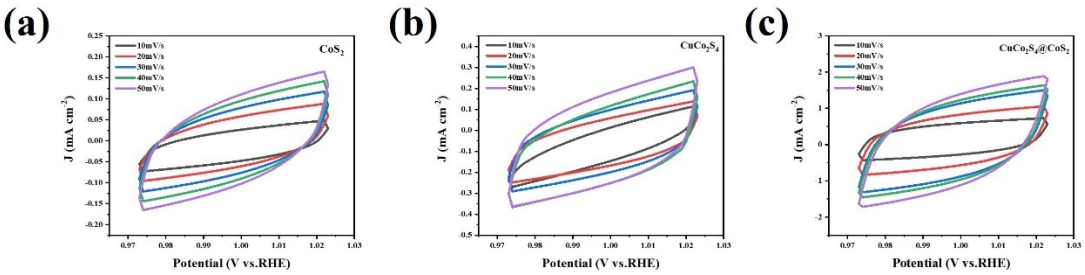

Fig S4. OER cyclic voltammetry of CoS_2 (a); $CuCo_2S_4$ (b); and $CuCo_2S_4$@CoS_2(c).

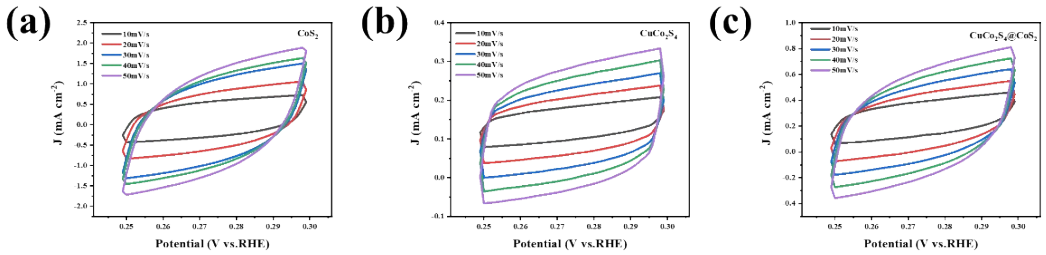

Fig S5. HER cyclic voltammetry of CoS_2 (a); $CuCo_2S_4$ (b); and $CuCo_2S_4$@CoS_2(c).

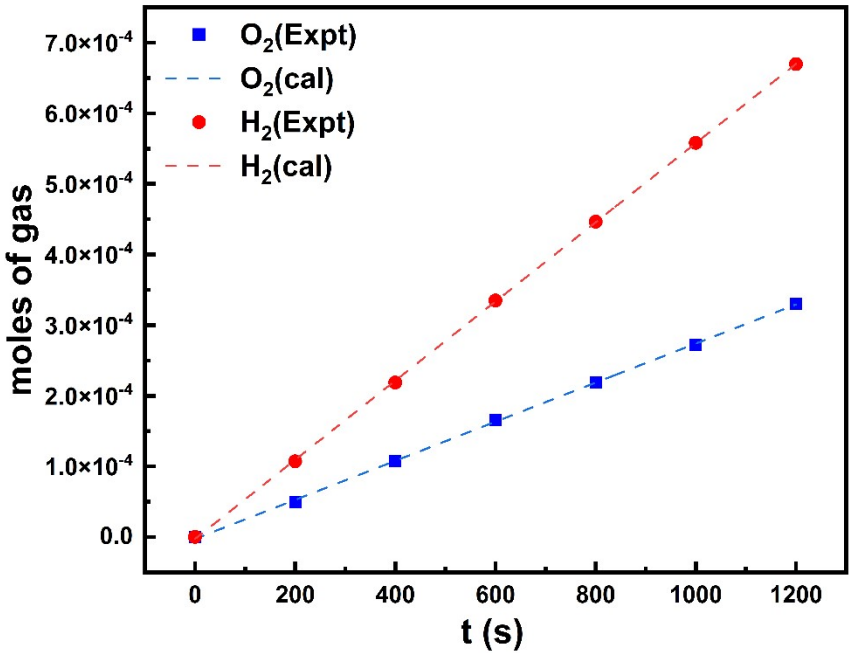

Figure S6. Faradic current efficiency for the HER and OER of the $CuCo_2S_4$@CoS_2 electrode measured at 110 $mAcm^{-2}$ in a 1M KOH aqueous electrolyte using conventional water displacement. The active electrode area of the cathode and anode was 0.9 cm^{-2}.

Table S1. Comparison of OER performances of $CuCo_2S_4@CoS_2$ with other reported electrocatalysts.

Catalyst	η_{10} (mV)	b (mV dec^{-1})	Electrolyte	Ref.
$CuCo_2S_4@CoS_2$	261	89.2	1.0 M KOH	This work
Co_3O_4/CoS_2	280	63	1.0 M KOH	[1]
$CuCo_2S_4/NiCo_2S_4$	271	57	1.0 M KOH	[2]
CoS_2 nanoboxes	290	72.2	1.0 M KOH	[3]
$CuCo_2S_4$ UNS	269	41	1.0 M KOH	[4]
CoO/CoS_2	320	77	1.0 M KOH	[5]
Ni-Doped CoS_2	270	79	1.0 M KOH	[6]
Ni-Fe-OH/Ni3S2/NF	268	54	1.0 M KOH	[7]
CoS_2/CoS	269	52	1.0 M KOH	[8]
$CuCo_2S_4/Fe_2O_3$	273	67	1.0 M KOH	[9]

Table S2. Comparison of HER performances of $CuCo_2S_4@CoS_2$ with other reported electrocatalysts.

Catalyst	η_{10} (mV)	b (mV dec^{-1})	Electrolyte	Ref.
$CuCo_2S_4@CoS_2$	153	151.7	1.0 M KOH	This work
CoS_2/MoS_2	177	66	1.0 M KOH	[10]
$CuCo_2S_4/NiCo_2S_4$	206	90	1.0 M KOH	[2]
$FeCo_2S_4$-$NiCo_2S_4$	150	38	1.0 M KOH	[11]
Sn-CoS_2/CC	161	94	1.0 M KOH	[12]
CoS_2/RGO	180	90	1.0 M KOH	[13]
$CoS_2@Co_3O_4$	320	42	1.0 M KOH	[14]
$MoS_2/NiCo_2S_4$	139	37	1.0 M KOH	[15]
CoS_2 HNSs	193	100	1.0 M KOH	[16]

Table S3. Comparison of the performances for water splitting system in this work with other reported electrocatalysts.

Catalyst	Cell voltage (V, @10 mA cm^{-2})	Stability (h)	Electrolyte	Ref.
$CuCo_2S_4$@CoS_2	1.61	20	1.0M KOH	This work
$CuCo_2S_4$/$NiCo_2S_4$	1.66	50	1.0 M KOH	[2]
$CuCo_2S_4$	1.66	24	1.0 M KOH	[17]
CoS_2-MoS_2	1.61	10	1.0 M KOH	[18]
Cu-CoP NAs/CP	1.72	60	1.0 M KOH	[19]
Cu_2S-Ni_3S_2	1.77	100	1.0 M KOH	[20]
O-CoMoS	1.6	10	1.0 M KOH	[21]
Co_9S_8@MoS_2	1.67	16	1.0 M KOH	[22]
MoS_2-NiS_2/NGF/NF	1.64	24	1.0 M KOH	[23]

[1] Guo M, Xu K, Qu Y, Zeng F, Yuan C. Porous Co_3O_4/CoS_2 nanosheet-assembled hierarchical microspheres as superior electrocatalyst towards oxygen evolution reaction. Electrochimica Acta. 2018;268:10-9.

[2] Ma L, Liang J, Chen T, Liu Y, Li S, Fang G. 3D $CuCo_2S_4$/$NiCo_2S_4$ core-shell composites as efficient bifunctional electrocatalyst electrodes for overall water splitting. Electrochimica Acta. 2019;326:135002.

[3] Guo X, Liang G, Gu A. Designed formation of CoS_2 nanoboxes with enhanced oxygen evolution reaction electrocatalytic properties. International Journal of Hydrogen Energy. 2019;44:31020-8.

[4] Hao Z, Wei P, Yang Y, Sun J, Song Y, Guo D, et al. Self-assembled $CuCo_2S_4$ nanosheets with rich surface Co^{3+} as efficient electrocatalysts for oxygen evolution reaction. Applied Surface Science. 2021;536:147826.

[5] Qin T, Ding Y, Zhang R, Gao X, Tang Z, Liu Y, et al. Bifunctional CoO/CoS_2 hierarchical nanospheres electrocatalyst for rechargeable Zn-Air battery. FlatChem. 2022;32:100343.

[6] Xie Z, Tang H, Wang Y. MOF-Derived Ni-Doped CoS_2 Grown on Carbon Fiber Paper for Efficient Oxygen Evolution Reaction. ChemElectroChem. 2019;6:1206-12.

[7] He W, Ren G, Li Y, Jia D, Li S, Cheng J, et al. Amorphous nickel–iron hydroxide films on nickel sulfide nanoparticles for the oxygen evolution reaction. Catalysis Science & Technology. 2020;10:1708-13.

[8] Hu X, Tan P, Dong R, Jiang M, Lu L, Wang Y, et al. A Novel Metal–Organic Framework

Intermediated Synthesis of Heterogeneous CoS_2/CoS Porous Nanosheets for Enhanced Oxygen Evolution Reaction. Energy Technology. 2021;9:2000961.
[9] Lu M, Zhang X, Tong J, Wang W, Wang Y. Enhanced Electron Transfer and Ion Transport by Binary and Multidimensional $CuCo_2S_4$/Fe_2O_3 on Carbon Cloth for Water Oxidation. Chemistry. 2021;27:238-41.
[10] Su C, Xiang J, Wen F, Song L, Mu C, Xu D, et al. Microwave Synthesized Three-dimensional Hierarchical Nanostructure CoS_2/MoS_2 Growth on Carbon Fiber Cloth: A Bifunctional Electrode for Hydrogen Evolution Reaction and Supercapacitor. Electrochimica Acta. 2016;212:941-9.
[11] Li D, Liu Z, Wang J, Liu B, Qin Y, Yang W, et al. Hierarchical trimetallic sulfide $FeCo_2S_4$–$NiCo_2S_4$ nanosheet arrays supported on a Ti mesh: An efficient 3D bifunctional electrocatalyst for full water splitting. Electrochimica Acta. 2020;340:135957.
[12] Liu F, He W, Li Y, Wang F, Zhang J, Xu X, et al. Activating sulfur sites of CoS_2 electrocatalysts through tin doping for hydrogen evolution reaction. Applied Surface Science. 2021;546:149101.
[13] Yang Y, Li F, Li W, Gao W, Wen H, Li J, et al. Porous CoS_2 nanostructures based on ZIF-9 supported on reduced graphene oxide: Favourable electrocatalysis for hydrogen evolution reaction. International Journal of Hydrogen Energy. 2017;42:6665-73.
[14] Aftab U, Tahira A, Samo AH, Abro MI, Baloch MM, Kumar M, et al. Mixed CoS_2@Co_3O_4 composite material: An efficient nonprecious electrocatalyst for hydrogen evolution reaction. International Journal of Hydrogen Energy. 2020;45:13805-13.
[15] Sun L, Wang T, Zhang L, Sun Y, Xu K, Dai Z, et al. Mace-like hierarchical MoS_2/$NiCo_2S_4$ composites supported by carbon fiber paper: An efficient electrocatalyst for the hydrogen evolution reaction. Journal of Power Sources. 2018;377:142-50.
[16] Ma X, Zhang W, Deng Y, Zhong C, Hu W, Han X. Phase and composition controlled synthesis of cobalt sulfide hollow nanospheres for electrocatalytic water splitting. Nanoscale. 2018;10:4816-24.
[17] Zequine C, Bhoyate S, Wang F, Li X, Siam K, Kahol PK, et al. Effect of solvent for tailoring the nanomorphology of multinary CuCo2S4 for overall water splitting and energy storage. Journal of Alloys and Compounds. 2019;784:1-7.
[18] Ganesan V, Kim J. Multi-shelled CoS_2–MoS_2 hollow spheres as efficient bifunctional electrocatalysts for overall water splitting. International Journal of Hydrogen Energy. 2020;45:13290-9.
[19] Yan L, Zhang B, Zhu J, Li Y, Tsiakaras P, Kang Shen P. Electronic modulation of cobalt phosphide nanosheet arrays via copper doping for highly efficient neutral-pH overall water splitting. Applied Catalysis B: Environmental. 2020;265:118555.
[20] Bhat KS, Nagaraja HS. In Situ Synthesis of Copper Sulfide-Nickel Sulfide Arrays on Three-Dimensional Nickel Foam for Overall Water Splitting. ChemistrySelect. 2020;5:2455-64.
[21] Hou J, Zhang B, Li Z, Cao S, Sun Y, Wu Y, et al. Vertically Aligned Oxygenated-CoS_2–MoS_2 Heteronanosheet Architecture from Polyoxometalate for Efficient and Stable Overall Water Splitting. ACS Catalysis. 2018;8:4612-21.
[22] Bai J, Meng T, Guo D, Wang S, Mao B, Cao M. Co_9S_8@MoS_2 Core-Shell Heterostructures as Trifunctional Electrocatalysts for Overall Water Splitting and Zn-Air Batteries. ACS Appl Mater Interfaces. 2018;10:1678-89.

[23] Kuang P, He M, Zou H, Yu J, Fan K. 0D/3D MoS_2-NiS_2/N-doped graphene foam composite for efficient overall water splitting. Applied Catalysis B: Environmental. 2019;254:15-25.