Supplementary Information

Rational design of Cu-Co thiospinel ternary sheet arrays for high efficient electrocatalytic water splitting

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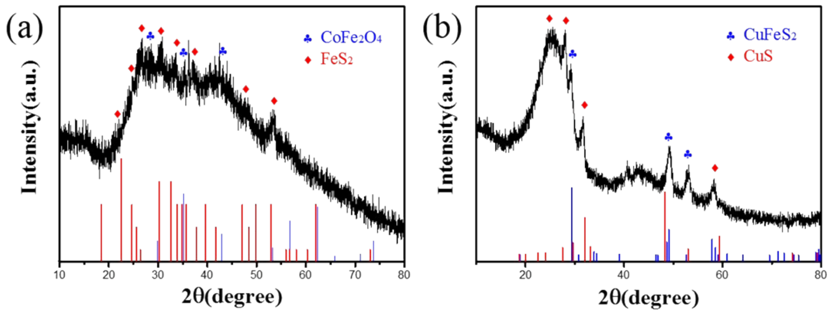

Fig. S1 The XRD patterns of $FeS_2/CoFe_2O_4$ (a) and $CuS/CuFeS_2$ (b) samples.

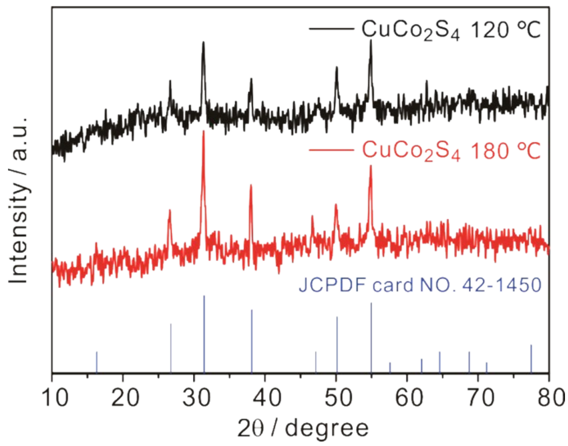

Fig. S2 The XRD patterns of $CuCo_2S_4$ TSA obtained at 120 °C and 180 °C.

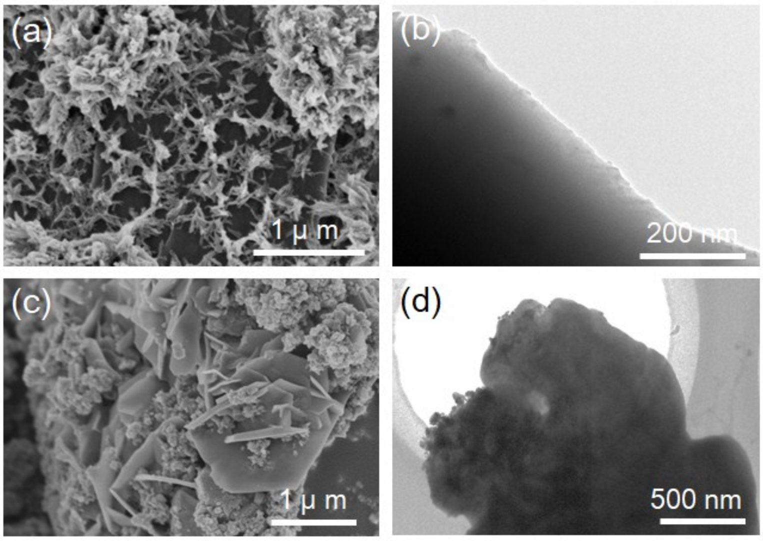

Fig. S3 The SEM (a) and TEM (b) images of $CuCo_2S_4$ TSA obtained at 120 °C; the SEM (c) and TEM (d) images of $CuCo_2S_4$ TSA obtained at 180 °C.

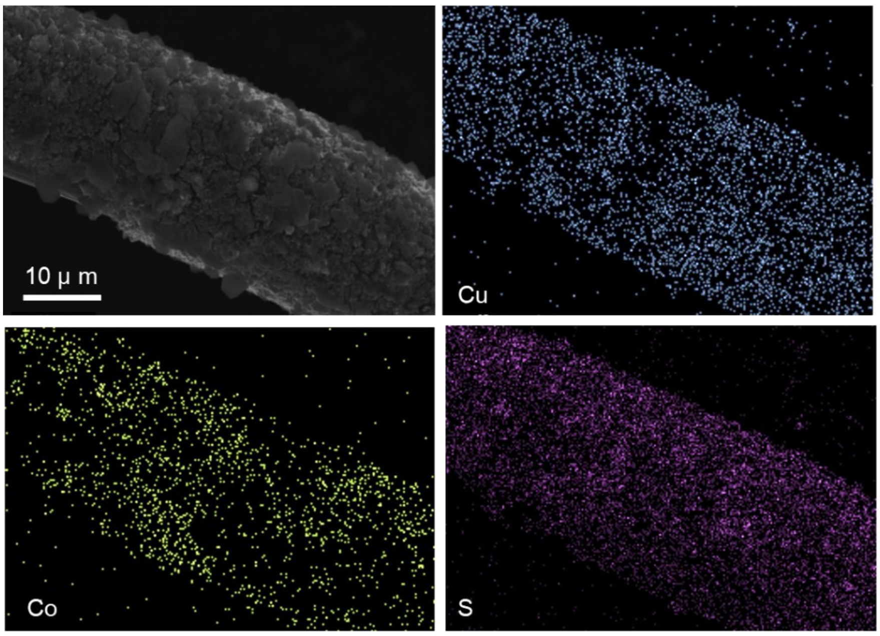

Fig. S4 SEM image of ternary $CuCo_2S_4$ TSA and the corresponding EDS mapping of Cu, Co, S elemental distribution.

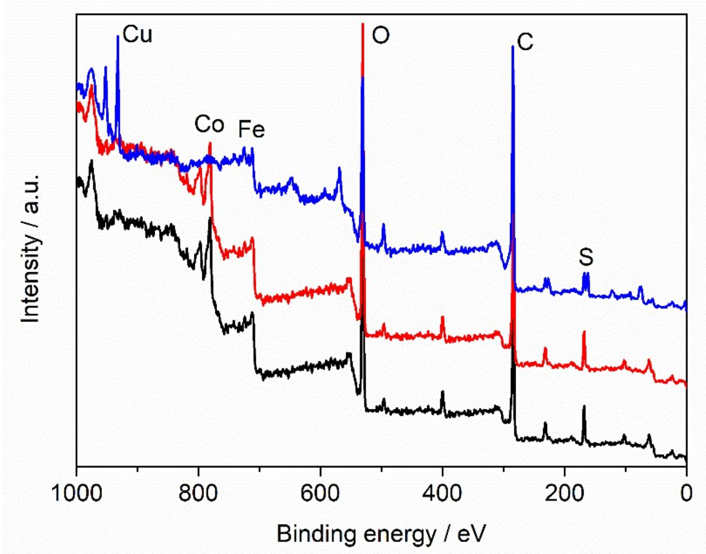

Fig. S5 The full range XPS spectra of $CuCo_2S_4$ TSA, $FeS_2/CoFe_2O_4$ and $CuS/CuFeS_2$ samples.

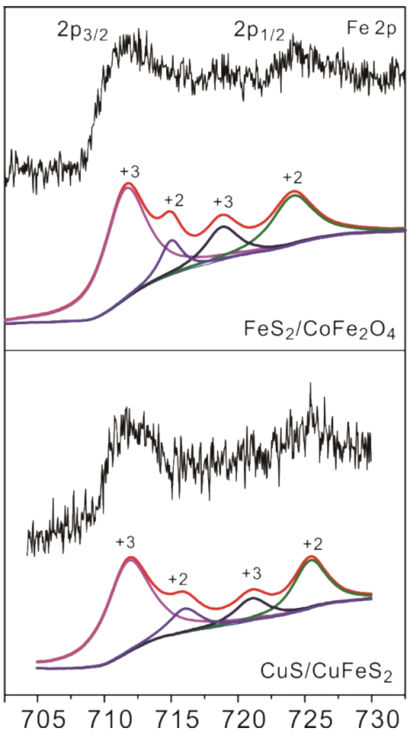

Fig. S6 High-resolution XPS spectra of the Fe 2p for $FeS_2/CoFe_2O_4$ and $CuS/CuFeS_2$ samples.

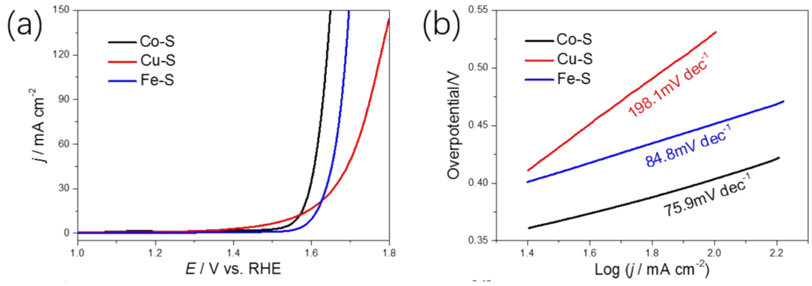

Fig. S7 (a) OER polarization curves of Co-S, Cu-S and Fe-S and the corresponding Tafel plots (b).

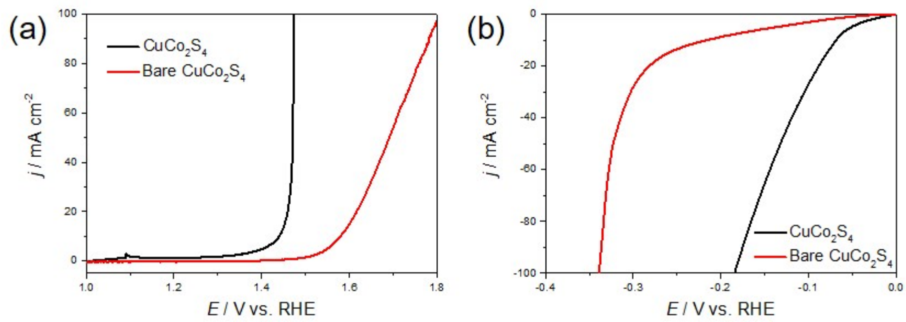

Fig. S8 OER (a) and HER (b) polarization curves of $CuCo_2S_4$ TSA and $CuCo_2S_4$ without carbon felt.

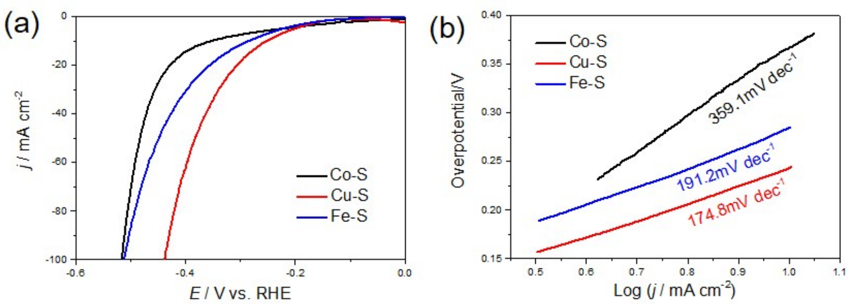

Fig. S9 (a) HER polarization curves of Co-S, Cu-S and Fe-S and the corresponding Tafel plots (b).

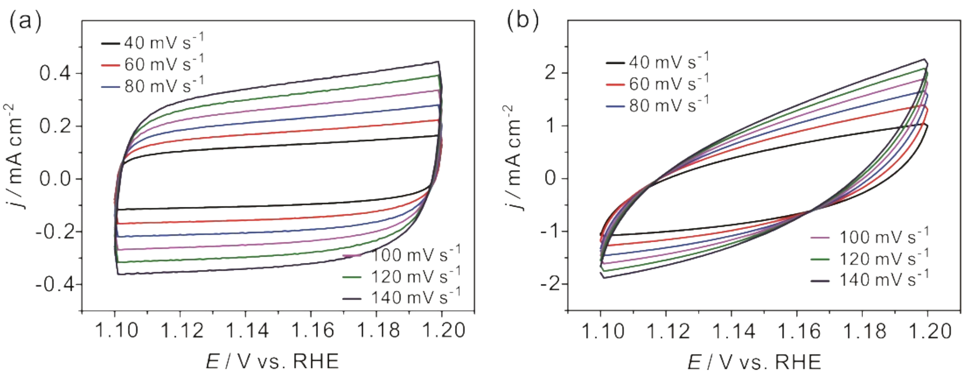

Fig. S10 Cyclic voltammograms of (a) CuS/$CuFeS_2$ and (b) FeS_2/$CoFe_2O_4$ with a potential window from 1.1 to 1.2 V at different scan rates in 1.0 M KOH.

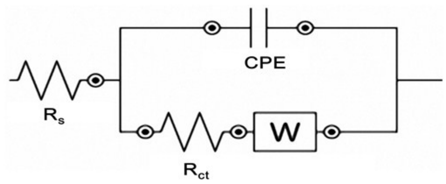

Fig. S11 Electrical equivalent circuit models for fitting the EIS response on the binary electrodes, where R_s is the solution resistance, R_{ct} represents the charge transfer resistance.

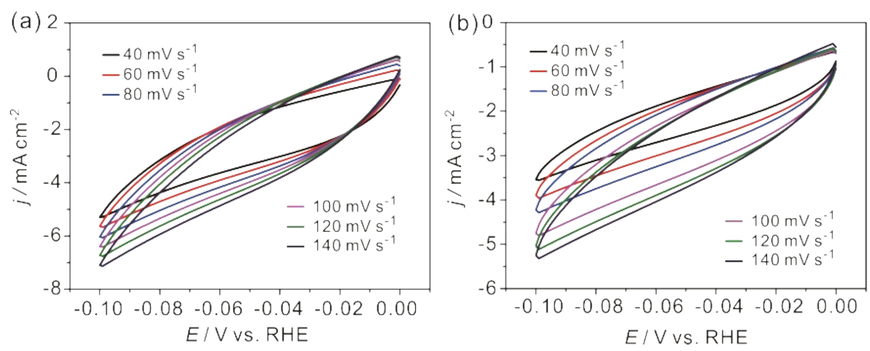

Fig. S12 Cyclic voltammograms of (a) CuS/$CuFeS_2$ and (b) FeS_2/$CoFe_2O_4$ with a potential window from -0.1 to 0 V at different scan rates in 1.0 M KOH.

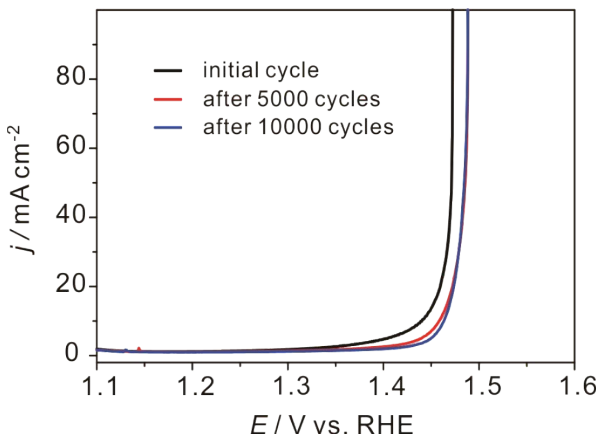

Fig. S13 LSV curves of $CuCo_2S_4$ nanoarrays electrode at the initial potential cycle and after 5000 and 10000 cycles.

Table S1. Comparative electrochemical OER performances of different electrocatalytic materials in alkaline medium.

Catalysts	Electrolyte	Overpotential (mV) @ 10 mA cm^{-2}	Tafel slope (mV dec^{-1})	Ref
$CuCo_2S_4$	1.0 M KOH	210	43.8	This work
CuS	1.0 M KOH	330	75.9	This work
$CuCo_2S_4$	1.0 M KOH	310	86	1
Co@Co_9S_8-180	1.0 M KOH	350	55	2
NiCo LDH nanosheets	1.0 M KOH	367	40	3
CoS_8 @MoS_2/CNFs	1.0 M KOH	430	61	4
CoMn-LDH	1.0 M KOH	324	43	5
$Zn_{0.3}Co_{2.7}O_4$	1.0 M KOH	389	61.57	6
$NiCo_2S_4$ NW/NF	1.0 M KOH	260	40.1	7
A-$CoS_{4.6}O_{0.6}$ PNCs	1.0 M KOH	290	67	8
Co_9S_8@MoS_2	1.0 M KOH	340	49	9
TiO_2@Co_9S_8	1.0 M KOH	240	55	10
$FeNi_2S_4$/GA	1.0 M KOH	273	66	11
Co_9S_8/CNT/carbon cloth	0.1 M KOH	321	58	12
CP/CTs/CoS	1.0 M KOH	306	72	13
Ni_3S_2/NF	1.0 M KOH	260	/	14

Table S2. Comparative electrochemical HER performances of different electrocatalytic materials in alkaline medium.

Catalysts	Electrolyte	Overpotential (mV) @ 10 mA cm^{-2}	Tafel slope (mV dec^{-1})	Ref
$CuCo_2S_4$	1.0 M KOH	69	55.4	This work
FeS_2@C	1.0 M KOH	195	127	15
Nb_2Se_9 3	0.5M H_2SO_4	160	63.7	16
V-Ni_2P NSAs/CC	1.0 M KOH	85	95	17
Al-Ni_2P/TM	1.0 M KOH	129	98	18
3% CoS_2-7% CuS	1.0 M KOH	85	46	19
$NiCo_2S_4$/Ni_3S_2/Ni	1.0 M KOH	119	105.2	20
$NiCo_2S_4$/CC	1.0 M KOH	263	141	21
CoS_2 HNSs	1.0 M KOH	290	100	22
Ni_3FeN/carbon cloth	1.0 M KOH	105	61	23
MoS_2 -Ni_3S_2 Heteronanorod/NF	1.0 M KOH	98	61	24
CoP nanowire/carbon cloth	1.0 M KOH	110	129	25
Zn-Co-S/CFP	1.0 M KOH	234	109	26

Table S3. Comparative electrochemical overall water splitting performances of different electrocatalytic materials in alkaline medium.

Catalysts	Electrolyte	Overall voltage (V) @ 10 mA cm^{-2}	Ref
$CuCo_2S_4$	1.0 M KOH	1.48	This work
$NiCo_2S_4$@NiFe LDH/ NF	1.0 M KOH	1.6	27
EG/$Co_{0.85}$Se/NiFe LDH	1.0 M KOH	1.67	28
Ni_2P	1.0 M KOH	1.63	29
CoFe LDH-F	1.0 M KOH	1.63	30
$Ni_{2.5}Co_{0.5}$Fe/NF	1.0 M KOH	1.62	31
NiCoFe LTH/CC	1.0 M KOH	1.55	32
NiS/NF	1.0 M KOH	1.64	33
Ni_3Se_2	1.0 M KOH	1.65	34
CoMnO@CN	1.0 M KOH	1.8	35
NiFe LDH/NiO/Ni-CNT	1.0 M KOH	1.5	36
NiFeOx	1.0 M KOH	1.7	37

Calculations:

Exchange current density (i_{ex}) = RT/nFAϴ

Where, R is the universal gas constant (8.314J K^{-1} mol^{-1}), T reaction temperature (298 K), n is the number of electrons, F is Faraday constant (96485 C mol^{-1}), ϴ is resistance (calculated from EIS), and A is area (1 cm^{-2}).

Table S4 I_{ex} values for different electrocatalytic materials.

Catalysts	OER mA cm^{-2}	HER mA cm^{-2}
$CuCo_2S_4$	18.3	13.7
$FeS_2/CoFe_2O_4$	16.1	11.01
$CuS/CuFeS_2$	13.7	6.7

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