Electronic Supplementary information

Experimental Section

Materials: Ammonium persulfate ($(NH_4)_2S_2O_8$), Sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$), sodium hydroxide (NaOH), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), manganese nitrate tetrahydrate ($MnN_2O_6 \cdot 4H_2O$), cerous nitrate hexahydrate ($Ce(NO_3)_6 \cdot 6H_2O$), ferric nitrate nonahydrate ($Fe(NO_3)_2 \cdot 9H_2O$) and nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) were purchased from Chengdu Kelong Chemical Reagent Factory. $RuCl_3 \cdot 3H_2O$, and Nafion (5 wt%) solution were obtained from Sigma–Aldrich Chemical Reagent Co., Ltd.. Cu foam (CF) was purchased from Shenzhen Green and Creative Environmental Science and Technology Co., Ltd. Before use, CF was pretreated in 3M HCl solution then washed by DI water and ethanol for 3 times to remove the surface impurities. All above reagents and chemicals were used as received without further purification and the water used throughout all experiments was purified through a Millipore system.

Preparation of Cu₂S/CF: Firstly, $Cu(OH)_2$ nanowire array on Cu foam ($Cu(OH)_2$/CF) was prepared as precursor. Typically, a piece of Cu foam (3*4 cm) was immersed in 20 mL of solution containing 2 g of NaOH and 456 mg of $(NH_4)_2S_2O_8$ at room temperature for 20 min, followed by washing with DI water for several times and drying in oven at 80 ℃ for 12 h. Then Cu₂S/CF was prepared through a facile ion exchange reaction of $Cu(OH)_2$/CF. In which, a piece of Cu foam with $Cu(OH)_2$ nanowire was immersed in 20 mL ethanol containing 180 mg of $Na_2S \cdot 9H_2O$ (dissolved by ultrasonication for 30 minutes) at room temperature for 1 h. After reaction，the sample was rinsed with DI water and ethanol and then dried in oven at 80 ℃ for 12 h.

Preparation of metal oxides on Cu₂S/CF : The deposition of metal oxides on surface of Cu₂S was conducted by a method[1] reported with modification. For Cu₂S-CoO$_x$/CF, typically, 0.1 mmol $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 10 mL of ethanol. Then 150 μL of metal precursor solution was speared on the surface of Cu₂S/CF (1*1 cm) and dried naturally. At last, the Cu₂S/CF loaded with metal precursor was annealed at 280 ℃ in Ar atmosphere for 3 h, through which, the metal nitrate salts decomposed to

metal oxides. For comparing, different amounts of Co precursor solution (50, 100, 150, 200 μL) were used in the progress. Besides, to investigate the electrochemical performance of Cu_2S/CF deposited with other metal oxides, different metal nitrate salts (Ce, Fe, Mn, Ni) were used in the above-mentioned process to prepare various metal oxides on Cu_2S/CF.

Preparation of metal oxides on CoS/CC: The CoS/CC was prepared firstly according to previous report.[2] Then 150 μL of metal precursor solution (Co, Ce and Ni) was coated on CoS/CC (1*1 cm). At last, the CoS/CC loaded with metal precursor was annealed at 280 ℃ in Ar atmosphere for 3 h.

Preparation of RuO₂: RuO_2 was prepared according to previous report[3]. Specifically, 2.61 g of $RuCl_3·3H_2O$ was dissolved in 100 mL DI water under stirring for 10 min at 100 ℃ followed by addition of 30 mL of 1 M NaOH solution. After stirred for 45 min at 100 ℃, the precipitates was collected and washed with DI water several times then dried at 80 ℃ overnight. Finally, the precipitates were annealed at 350 ℃ for 1 h in air atmosphere to obtain crystalline RuO_2. As–prepared RuO_2 powder (0.01 g) was dispersed into a solution of Nafion, ethanol and ultrapure water with a volume ratio of 10/250/250 *via* sonication, and then deposited onto Cu Foam(1*1cm) with a mass loading of 4 mg cm^{-2}.

Characterizations: X–ray diffraction (XRD) measurements were operated on a Panaiytical/Empyrean. Scanning electron microscope (SEM) images were photographed on a JSM–7500F. Transmission electron microscopy (TEM) images were collected on a Tecnai G2 F20 S-TWIN. X–ray photoelectron spectroscopy (XPS) patterns were measured on an AXIS Ultra DLD X–ray photoelectron spectrometer using Al as the excitation source.

*Electrochemical measurements: All e*lectrochemical measurements were conducted on a DH7000 electrochemical workstation (Jiangsu Donghua Analytical Instruments Co., Ltd.) in 1 M KOH at 25 ℃. The Cu_2S-CoO_x/CF, platinum plate and Hg/HgO were performed as working electrode, counter electrode and reference electrode respectively in a standard three–electrode system. The linear sweep voltammetry (LSV) and cyclic voltammetry (CV) measurements were carried out with scan rate of 5 mV s^{-1} and 100

mV s^{-1} respectively. Potentials were calibrated to RHE unless especially stated according to the following equation: E (RHE) = E (Hg/HgO) + (0.098+ 0.0591*pH) V.

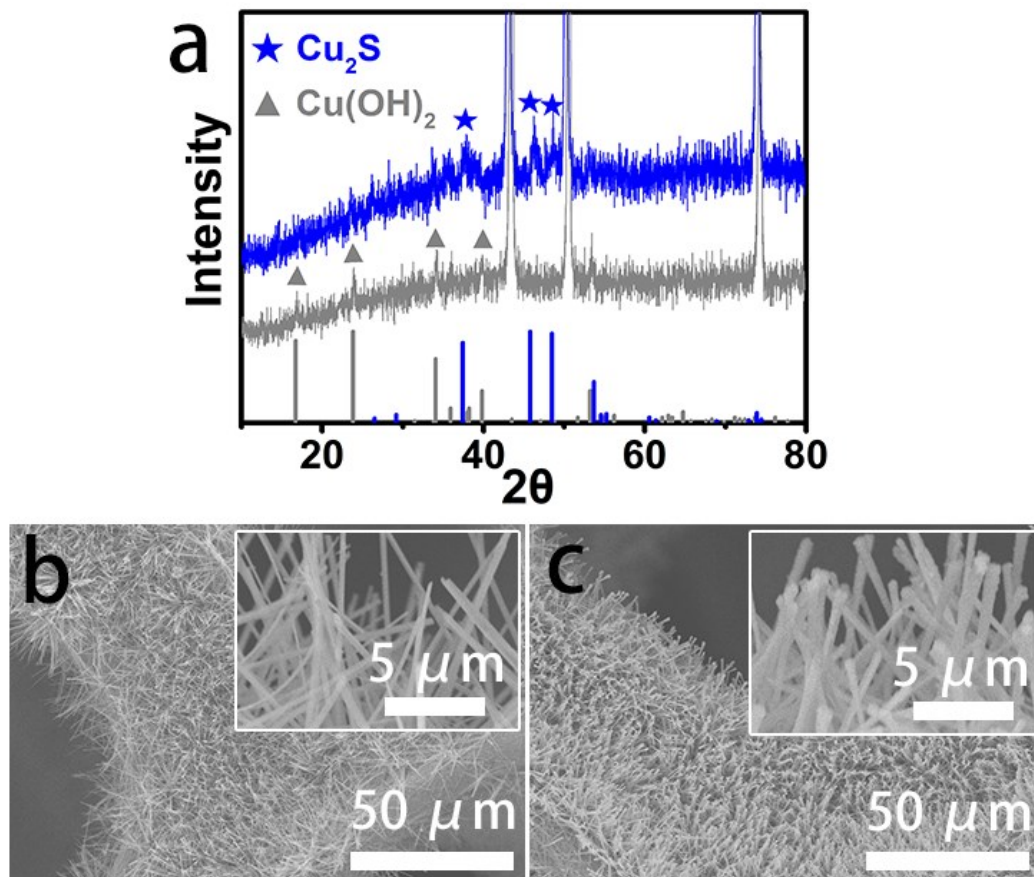**Figure S1.** (a) XRD patterns of Cu(OH)$_2$/CF and Cu$_2$S/CF, SEM images for (b) Cu(OH)$_2$/CF and (c) Cu$_2$S/CF.
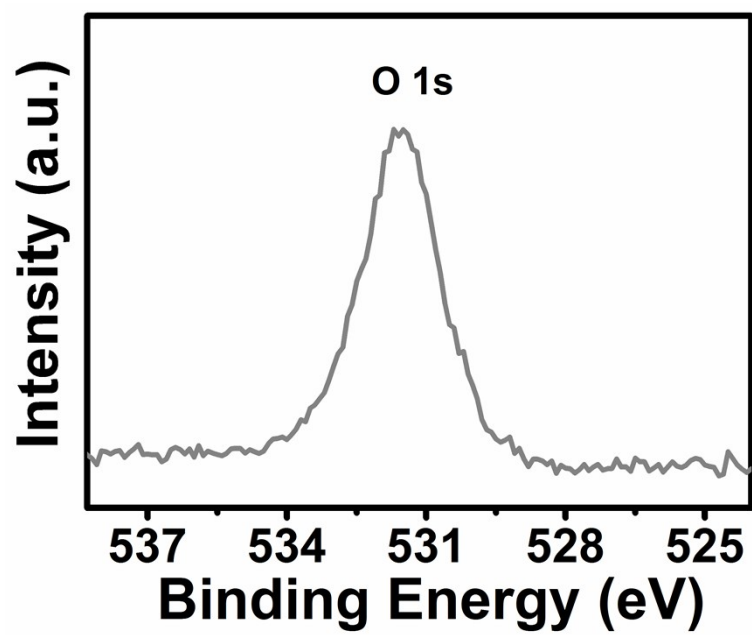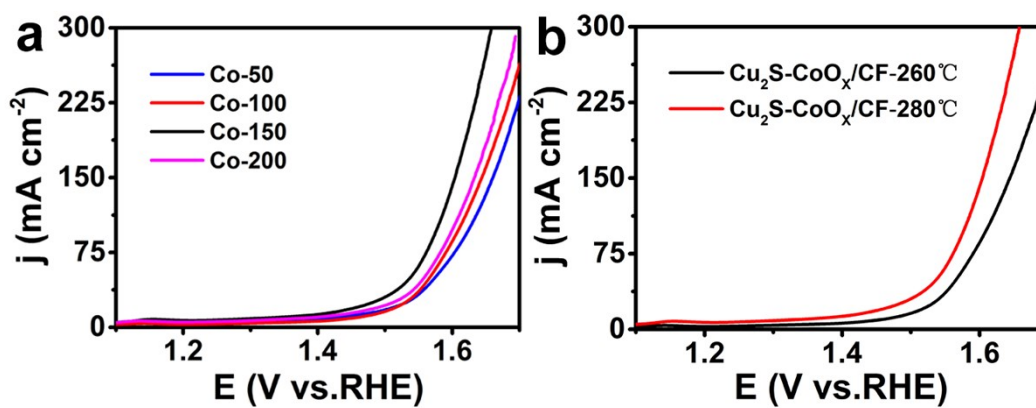
Figure S2. XPS spectra for O 1s in Cu_2S-CoO_x/CF.

Figure S3. (a) LSV curves of Cu$_2$S/CF coated with 50, 100, 150 and 200 µL of Co precursor solution followed by annealing in 280 ℃, (b) LSV curves of Cu$_2$S/CF coated with 150 µL of Co precursor solution followed by annealing in 260 and 280 ℃.
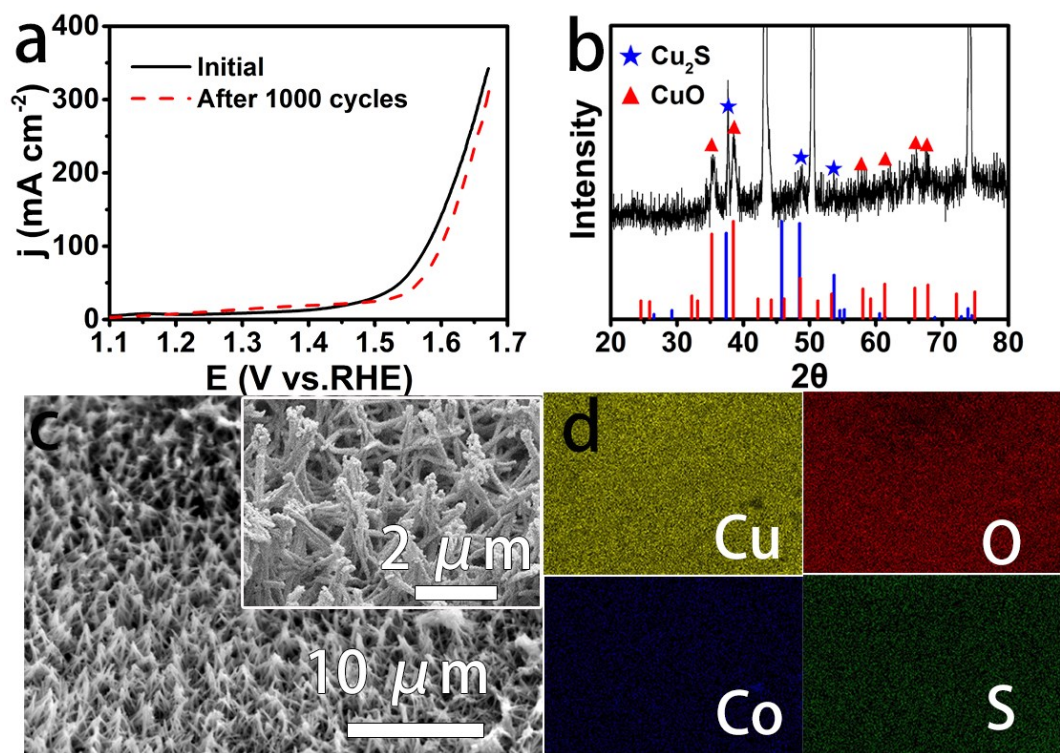
Figure S4. (a) LSV curve, (b) XRD pattern, (c) SEM images, and EDX elemental mapping images of Cu_2S-CoO_x/CF having undergone 1000 CV cycles.

Table S1. Comparison of OER performance for Cu_2S-CoO_x/CF with other metal sulfides working in alkaline condition.

Catalyst	j (mA cm^{-2})	η (mV)	Electrolyte	Ref.
Cu_2S-CoO_x/CF	25	255	1.0 M KOH	This work
Cu_2S/CF nanosheet arrays	20	336	1.0 M KOH	4
MoS_2/NiS_2-3 nanonsheet	10	278	1.0 M KOH	5
Ni_3S_2/MnO_2 nanoarrays	10	260	1.0 M KOH	6
CeO_x/CoS	10	269	1.0 M KOH	7
FeS-NiS	10	260	1.0 M KOH	8
Ni_3S_2/NiS	10	298	1.0 M KOH	9
CoS nanowires	10	293	1.0 M KOH	10
CoS_x	10	375	1.0 M KOH	11
NiS_2/$NiSe_2$	20	290	1.0 M KOH	12
Ni-Co sulfide	10	272	1.0 M KOH	13
Co/Ce-Ni_3S_2/NF	20	286	1.0 M KOH	14
meso-Fe-MoS_2/$CoMo_2S_4$	10	290	1.0 M KOH	15
MnS	10	292	1.0 M KOH	16
CoS_x/FeS_x	10	304	1.0 M KOH	17

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