Electronic Supplementary Information

Experimental section

Materials: Carbon Cloth was provided by Hongshan District, Wuhan Instrument Surgical Instruments business. $CuCl_2 \cdot 2H_2O$ and urea were purchased from Beijing Chemical Works. $CoCl_2 \cdot 6H_2O$ was purchased from Aladdin Ltd. (Shanghai, China). Nafion (5 wt%) and Pt/C were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. The water used throughout all experiments was purified through a Millipore system. All the reagents and chemicals were used as received without further purification.

Synthesis of Cu_3P-CoP/CC, CoP/CC, and Cu_3P/CC: The precursor was prepared as follows. $CoCl_2 \cdot 6H_2O$ (2.5 mmol), $CuCl_2 \cdot 2H_2O$ (1.25 mmol) and urea (11.25 mmol) were dissolved in 30 mL distilled water. After gentle stirring for 15 min, the clear solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and a piece of CC (2 cm × 4 cm) which was cleaned by sonication in water and ethanol for 10 min was immersed into the solution. The autoclave was sealed and maintained at 120 °C for 6 h in an electric oven. After the autoclave cooled down at room temperature, the resulting precursor was taken out and washed with water and ethanol several times, followed by drying at 60 °C. After that, the precursor was placed in a porcelain boat and the other porcelain boat containing 1.0 g NaH_2PO_2 was placed at the upstream of the tube furnace. The two porcelain boats were calcined at 300 °C for 2 h with a heating speed of 2 °C min^{-1} under Ar flow and then cooled down to room temperature naturally. CoP/CC was prepared as follows: $CoCl_2 \cdot 6H_2O$ (2.5 mmol), and urea (11.25 mmol) were dissolved in 30 mL distilled water, the other steps are same as above, and Cu_3P/CC was prepared as follows: $CuCl_2 \cdot 2H_2O$ (1.25 mmol) and urea (11.25 mmol) were dissolved in 30 mL distilled water, the other steps are same as above.

Preparation of Pt/C electrode: To prepare Pt/C electrode, 20 mg Pt/C and 10 μL 5 wt% Nafion solution were dispersed in 1 mL 1:1 v water/ethanol solvent by 30 min sonication to form an ink finally. Then 104 μL catalyst ink was loaded on bare CC with a catalyst loading of 2.05 mg cm^{-2}.

Characterizations: The X-ray diffraction (XRD) patterns were obtained from a LabX XRD-6100 X-ray diffractometer with Cu Kα radiation (40kV, 30mA) of wavelength 0.154 nm (SHIMADZU, Japan). Scanning electron microscope (SEM) measurements were recorded on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. The structures of the samples were determined by Transmission electron microscopy (TEM) images on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) data of the samples was collected on an ESCALABMK II x- ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system. Cu_3P-CoP/CC and a graphite plate was used as the working electrode and the counter electrode, respectively. Ag/AgCl electrode and Hg/HgO electrode were used as the reference electrode in 0.5 M H_2SO_4 and 1.0 M KOH, respectively. All tests were carried out at room temperature. The potentials reported in this work were calibrated to RHE other than especially explained. In 0.5 M H_2SO_4, E (RHE) = E (Ag/AgCl) + (0.197 + 0.059pH) V. In 1.0 M KOH, E (RHE) = E (Hg/HgO) + (0.098 + 0.059pH) V.

Calculated electrochemical active surface area (ECSA)[1]:

$$A_{ECSA} = \frac{C_{dl}}{40\ \mu F\ cm^{-2}\ \text{per}\ cm^2_{ECSA}}$$

To calculate the turnover frequency (TOF), we used the following formula[1]:

$$TOF = \frac{\left(3.12 \times 10^{15} \times \frac{H_2/_S}{cm^2}\ \text{per}\ \frac{mA}{cm^2}\right) \times j}{\text{surface sites} \times A_{ECSA}}$$

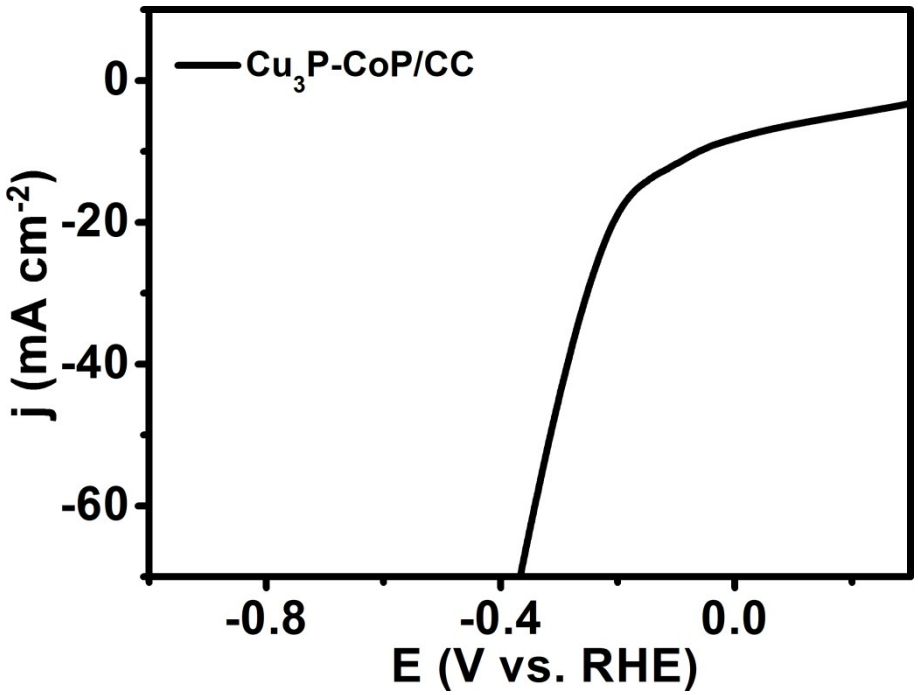

Fig. S1. LSV curves for Cu_3P–CoP/CC with a scan rate of 5 mV s^{-1} in 1.0 M KOH**.**

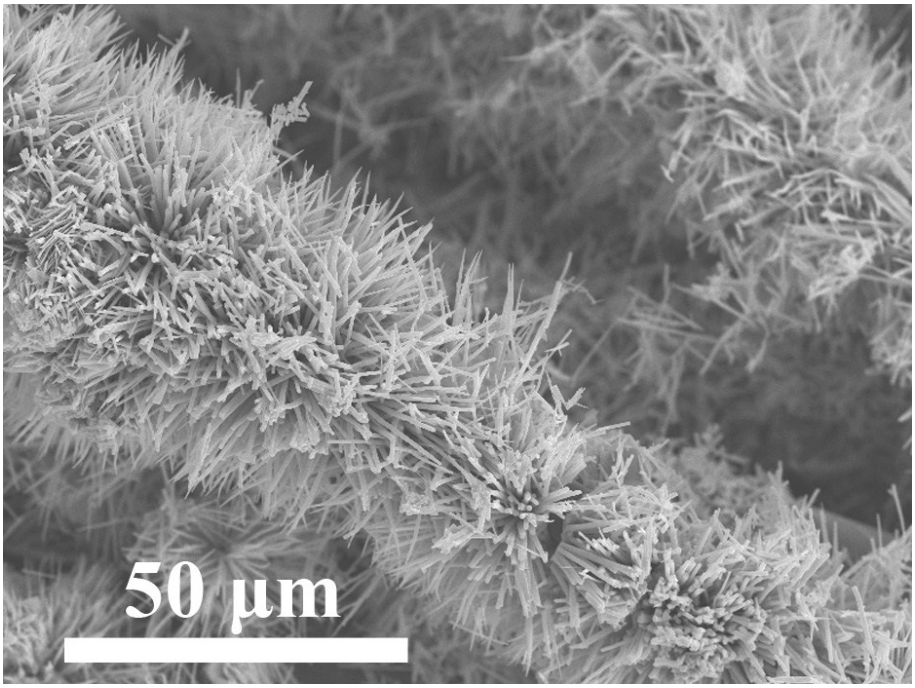

Fig. S2. SEM image of Cu_3P-CoP/CC after 500 cyclic voltammetry cycles.

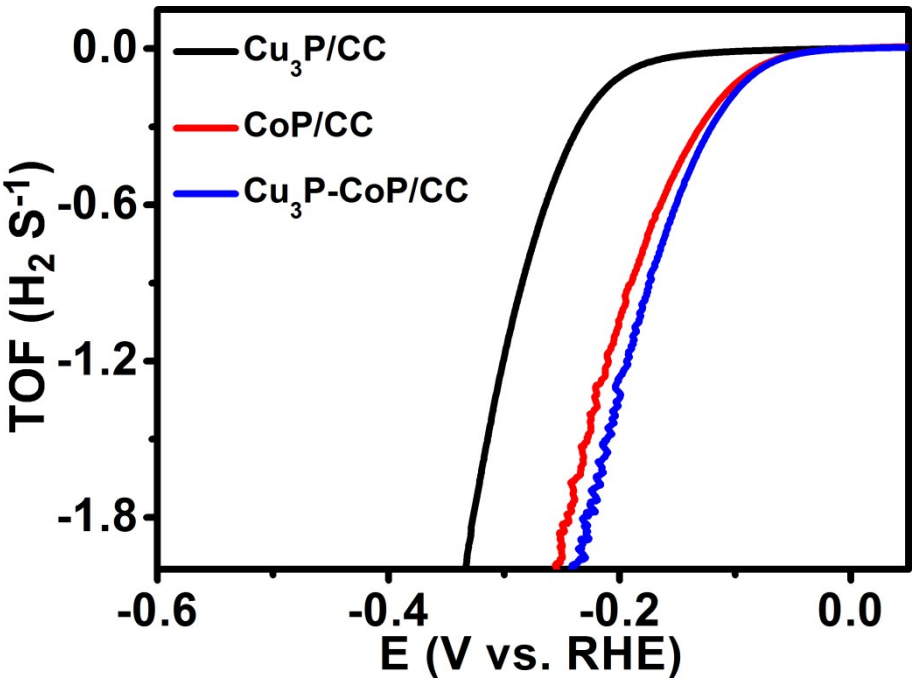

Fig. S3. TOF calculation of Cu_3P/CC, CoP/CC and Cu_3P-CoP/CC.

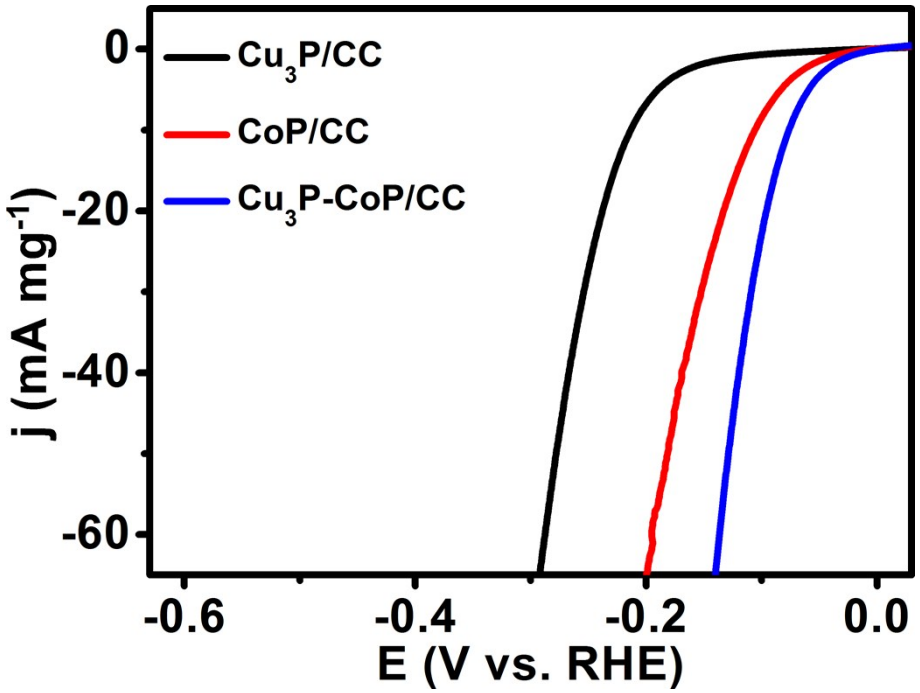

Fig. S4. Mass-normalized polarization curves for Cu_3P/CC, CoP/CC and Cu_3P-CoP/CC in 0.5 M H_2SO_4.

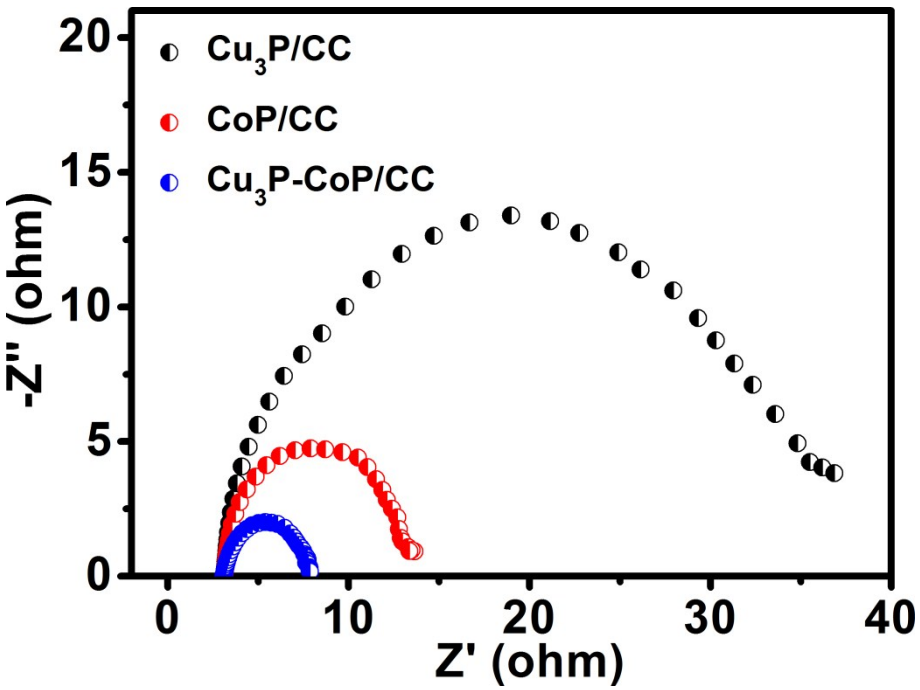

Fig. S5. Nyquist plots of Cu_3P/CC, CoP/CC and Cu_3P-CoP/CC recorded in 0.5 M H_2SO_4.

Table S1. Comparison of HER performance for Cu_3P-CoP/CC with other non-noble-metal electrocatalysts in 0.5 M H_2SO_4.

Catalyst	j (mA cm^{-2})	Overpotential (mV)	Ref.
Cu_3P-CoP/CC	10	59	This work
CoP/CC	10	83	
Cu_3P/CC	10	189	
CoP/CNT	10	122	2
CoP/Ti	10	90	3
CoP NRAs	10	~181	4
CoP	10	85	5
CoP/NCNTs	10	383	6
CoP nanowire/CC	10	67	7
CoP hollow polyhedron	10	159	8
Co_2P branched nanostructures	10	120	9
$Fe_{0.5}Co_{0.5}P$	10	130	10
C@NiCoP	10	276	11
CoP NWs	10	110	12
interconnected MoP nanoparticle	10	125	13
Cu_3P NW/CF	10	143	14
Cu_3P nanocubes	10	~300	15

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