

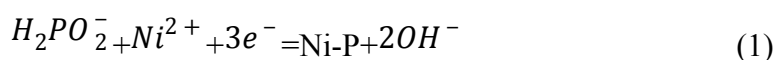
Electronic Supplementary Information

Experimental Section

Materials: $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ were purchased from Chengdu Kelong Chemical Reagent Factory. Sodium hydroxide (NaOH) and sodium citrate $(\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O})$ were purchased from Tianjin Rgent Chemical Co. Ltd. Ammonium persulfate (APS) was purchased from Xilong Chemical Co. Ltd (Guangzhou, China). Sodium hypophosphite $(\text{NaH}_2\text{PO}_2)$ was purchased from Aladdin Ltd (Shanghai, China). Copper foam (CF) was purchased from Alantum Advanced Technology Materials Co. Ltd (Dalian, China). The water used throughout all experiments was purified through a Millipore system. All chemicals were used as received without further purification.

Preparation of CuO NA/CF: First, $\text{Cu}(\text{OH})_2$ NA/CF was made according to the previous report.¹ In brief, copper foam was washed with diluted HCl and water several times to remove the surface impurities. Then a piece of CF was rapidly immersed into a 30 mL mixed solution (4 mmol APS and 80 mmol NaOH) at room temperature for 30 minutes. The resulting $\text{Cu}(\text{OH})_2$ NA/CF was dried at 60 °C for 12 h in vacuum oven for use. Last, $\text{Cu}(\text{OH})_2$ NA/CF was annealed at 250 °C for 1 h, the CuO NA/CF was obtained.

Preparation of CuO@Ni-P NA/CF: 1.19 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 3 g $(\text{NH}_4)_2\text{SO}_4$, 3 g $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ and 3 g NaH_2PO_2 were dissolved in 50 mL deionized water for use. To obtain CuO@Ni-P NA/CF, the CuO NA/CF (0.5 cm * 0.5 cm) electrode as the working electrode was polarized at -1.1 V (vs. SCE) in above solution for 2000 s, with the use of carbon rod as the auxiliary electrode and a SCE as the reference electrode. Phosphorus cannot be deposited alone, however, it can be deposited in the presence of a metal of the iron group such as nickel and this phenomenon is known as induced co-deposition.² According to the early studies,³ the deposition possible mechanism can be described as follows [Eq. (1)]:



Preparation of Pt/C and RuO₂ loaded electrodes: RuO₂ catalyst was prepared. In brief, 0.01 mol of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was dissolved in 100 mL deionized water and heated under air atmosphere at 100 °C for 10 min, followed by the addition of 1 mL of 1.0 M KOH solution. The reaction mixture was maintained at this temperature under stirring for 45 min. After that, the solution was centrifuged for 10 min and filtered. The precipitate was washed several times with deionized water to remove the remaining chlorides. The resulting Ru-hydroxide was dried for 5 h at 80 °C and then calcined in air at 300 °C for 3 h to obtain RuO₂. To prepare Pt/C and RuO₂ loaded electrodes, 12 mg Pt/C or RuO₂ and 50 μL 5 wt% Nafion solution were dispersed in 950 μL 1:1 v water/ethanol solvent by 30 min sonication to form an ink finally. Then 60 μL catalyst ink was loaded on CF with a catalyst loading of 2.9 mg cm⁻².

Characterizations: The XRD patterns were obtained from a LabX XRD-6100 X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). Scanning electron microscopy (SEM) measurements were

performed on a HITACHI S-4800 scanning electron microscope at an accelerating voltage of 25 kV. Transmission electron microscopy (TEM) measurements were made on a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. X-ray photoelectron spectrometer (XPS) measurements were performed 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 using CuO@Ni-P NA/CF as working electrode, carbon rod as the counter electrode, and a mercury/mercuric oxide electrode (Hg/HgO) used as the reference electrode. All potentials measured were calibrated to RHE using the following equation: $E \text{ (RHE)} = E \text{ (Hg/HgO)} + (0.059 * \text{pH} + 0.098) \text{ V}$. Polarization curves were obtained using linear sweep voltammetry with a scan rate of 5 mV s^{-1} . All experiments were carried out at room temperature ($\sim 25 \text{ }^{\circ}\text{C}$).

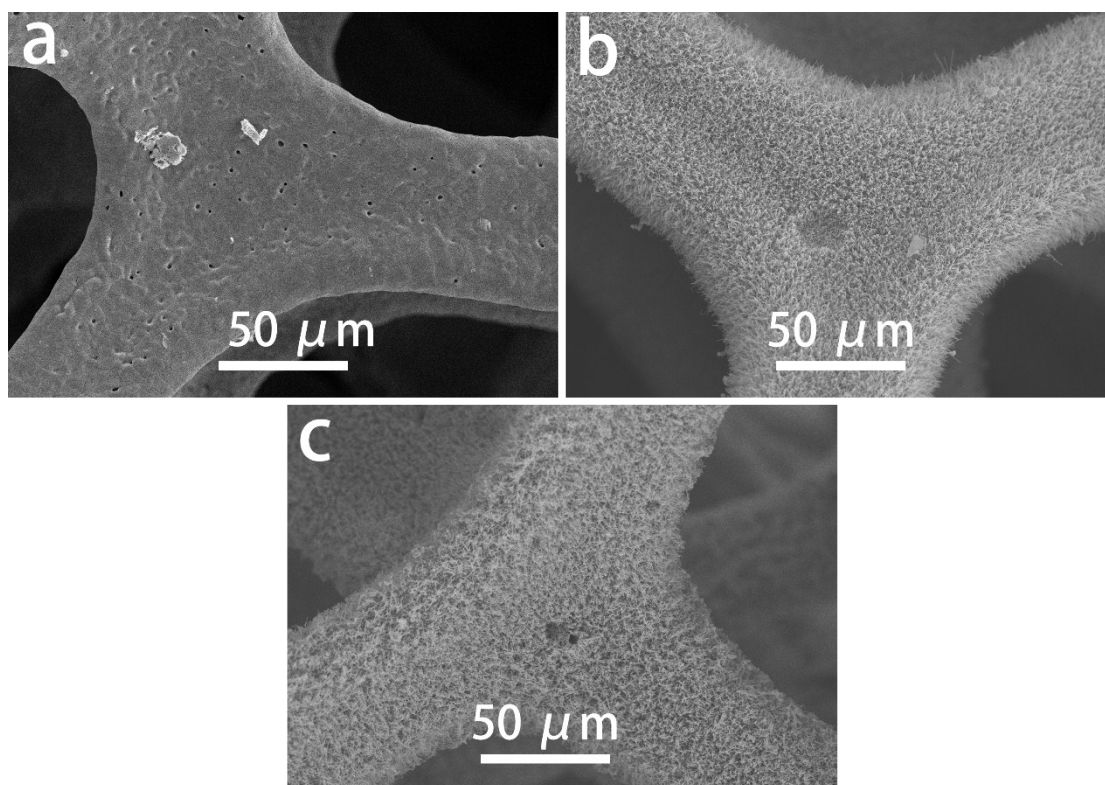


Fig. S1. SEM images for bare CF (a), CuO NA/CF (b), and CuO@Ni-P NA/CF (c).

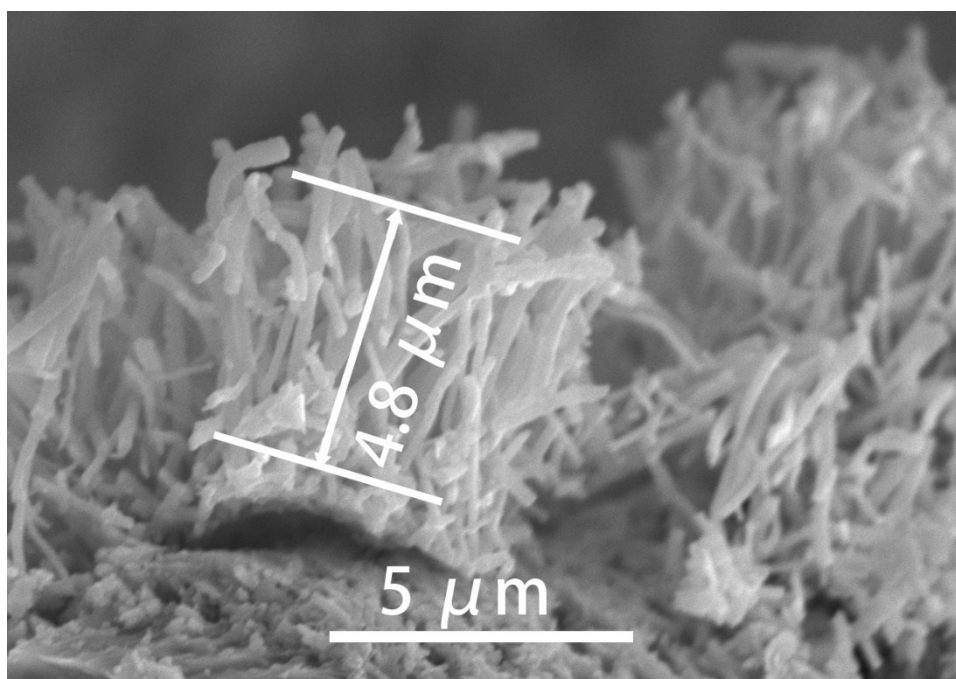


Fig. S2. Cross-section SEM image of CuO@Ni-P NA/CF.

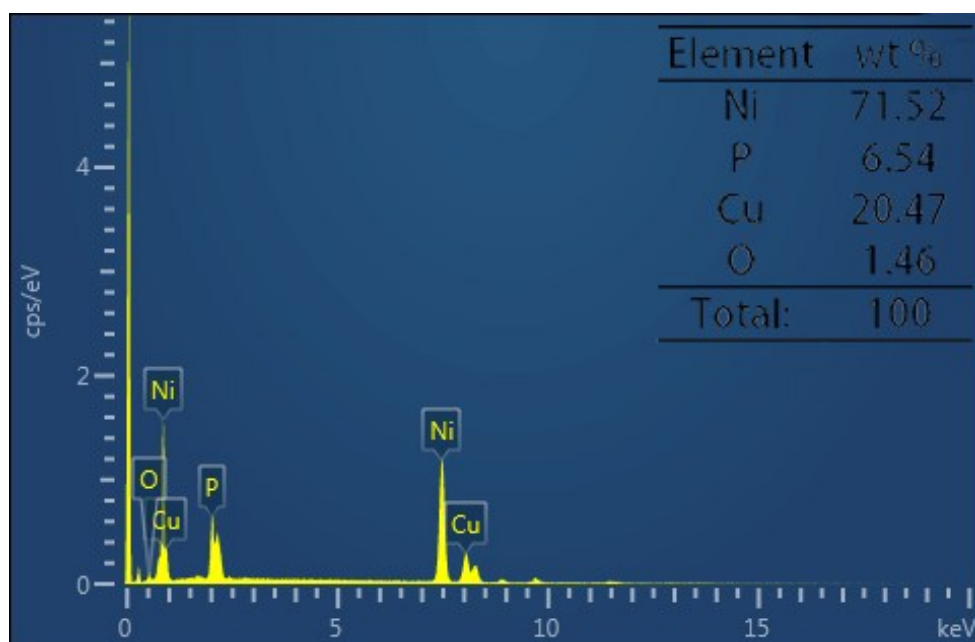


Fig. S3. EDX spectrum of CuO@Ni-P NA/CF.

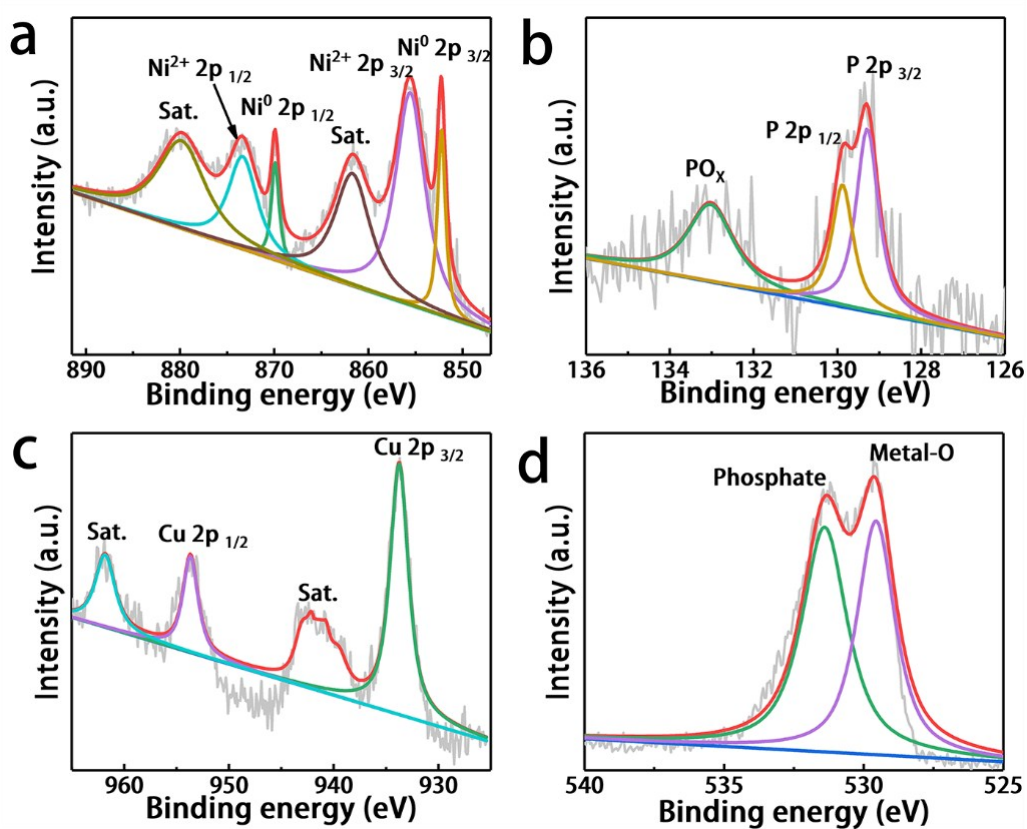


Fig. S4. XPS spectra of CuO@Ni-P NA/CF in the (a) Ni 2p, (b) P 2p, (c) Cu 2p, and (d) O 1s regions.

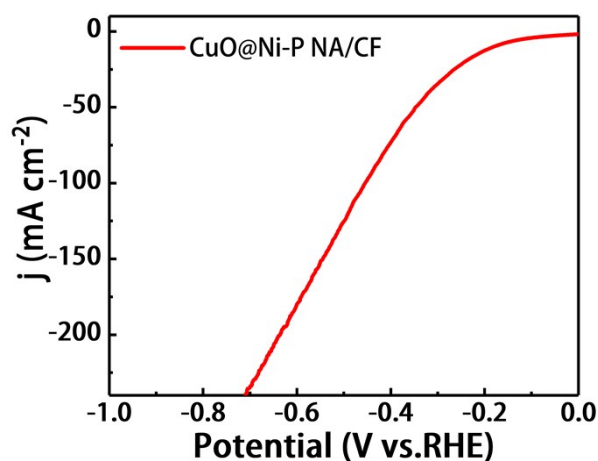


Fig. S5. LSV curves of CuO@Ni-P NA/CF for the HER in 0.1 M PBS (pH=7) with a scan rate of 5 mV s⁻¹.

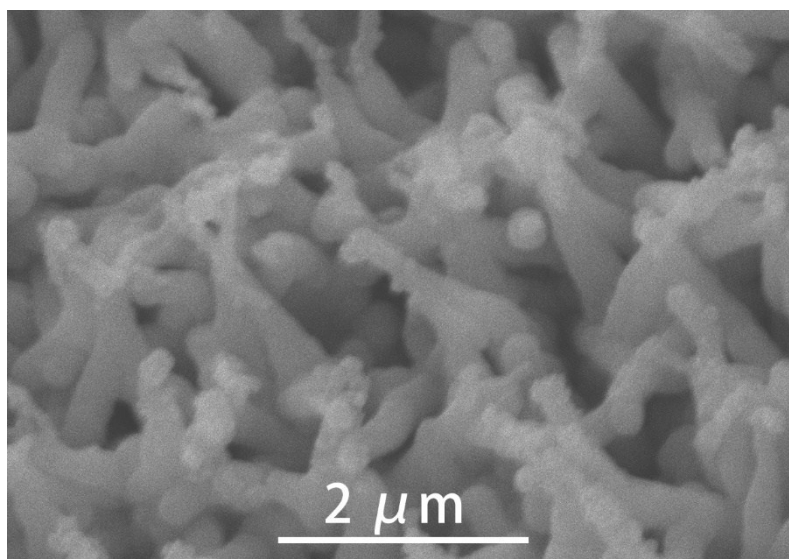


Fig. S6. SEM image of CuO@Ni-P NA/CF after 35 h test.

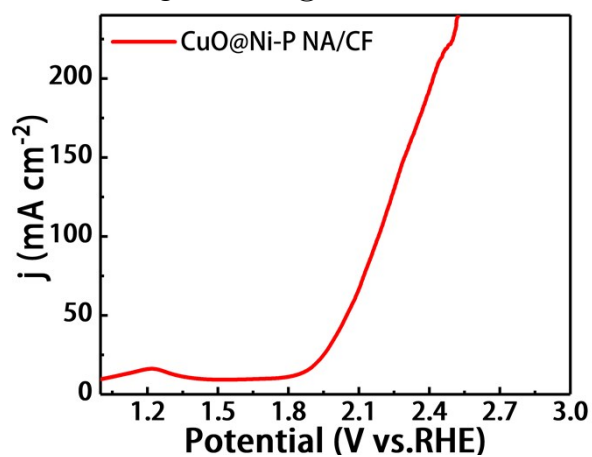


Fig. S7. LSV curves of CuO@Ni-P NA/CF for the OER in 0.1 M PBS (pH=7) with a scan rate of 5 mV s⁻¹.

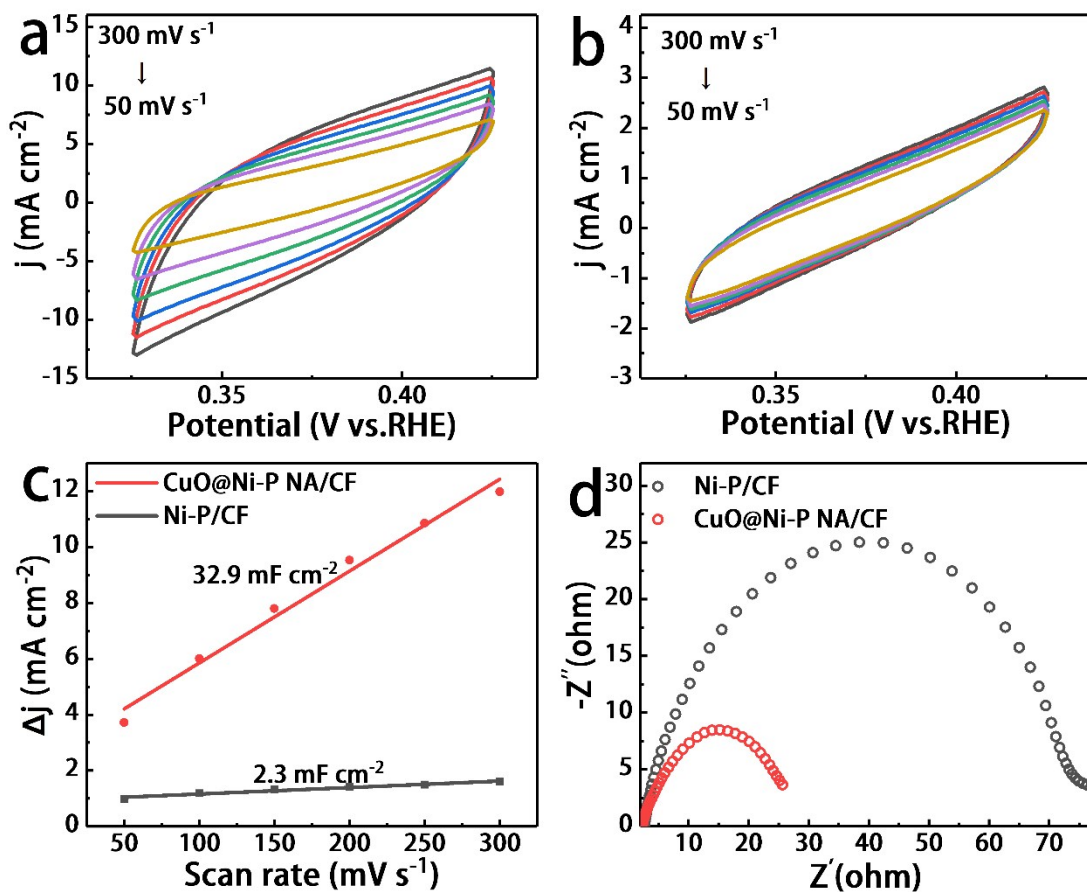


Fig.S8. CV curves for CuO@Ni-P NA/CF (a) and Ni-P/CF (b) at different scan rates: 50, 100, 150, 200, 250 and 300 mV s^{-1} from inside to outside. (c) Capacitive current at 0.325 V (vs. RHE) as a function of the scan rate for CuO@Ni-P NA/CF and Ni-P/CF ($\Delta j = j_a - j_c$). (d) Nyquist plots for CuO@Ni-P NA/CF and Ni-P/CF in frequency of 0.1-100 KHz.

Table S1. Comparison of HER performance for CuO@Ni-P NA/CF with other non-noble-metal electrocatalysts in alkaline media.

Catalyst	j (mA cm ⁻²)	η (mV)	Refs.
CuO@Ni-P NA/CF	10	73	This work
	30	106	
	100	147	
Ni ₂ P nanoparticles	10	230	4
NiO/Ni-CNT	10	~80	5
Ni ₃ N/NF	10	121	6
	100	254	
Ni ₃ S ₂ /NF	10	123	7
NiS ₂ /CC	10	149	8
Ni wire	10	350	9
Ni-Mo alloy/Ti	10	80	9
CoP/CC	10	209	10
Ni-Co-S/CF	10	140	11
WP NA/CC	10	150	12
WP ₂ submicroparticles	10	153	13
NiSe/NF	10	96	14
Ni@NiO/Cr ₂ O ₃	100	150	15
U-CNT-900	10	240	16
Co-NRCNT	10	370	17
MoC _x nano-octahedrons	10	150	18
MoS ₂ @Ni/CC	10	91	19
	100	196	

Table S2. Comparison of OER performance for CuO@Ni-P NA/CF with other non-noble-metal electrocatalysts in alkaline media.

Catalyst	j (mA cm ⁻²)	η (mV)	Refs.
CuO@Ni-P NA/CF	30	275	This work
	50	328	
	100	364	
NiO@Ni-Bi/CC	20	313	20
Ni/NiO	10	345	21
NiO on Ni foam	10	360	22
NiO _x /Ni	10	390	23
NiO@NF-6	10	405	24
β -Ni(OH) ₂	10	340	25
Ni(OH) ₂ on O-MWCNTs	10	310	26
β -Ni(OH) ₂ nanosheets	10	415	27
Ni(OH) ₂ /NF	20	372	28
Amorphous NiO	20	>470	29
NiO _x /C	10	335	30

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