

Electronic Supplementary Information

Experimental section

Materials: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NH_4F , urea, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, NaOH , $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, and KOH were purchased from Aladdin Ltd. (Shanghai, China). Nafion (5 wt%) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. All chemicals were used as received without further purification. Cu foil was purchased from Phychemsi Hong Kong Co., Ltd and was cleaned by sonication sequentially in acetone, water and ethanol several times to remove the surface impurities. The water used throughout all experiments was purified through a Millipore system.

Synthesis of CuO NW/CF: All the experiments were performed at ambient temperature of 25 °C. The cleaned Cu foil (CF) was used as the initial stock material for the succeeding reactions. In a typical procedure, a piece of CF (1 cm × 1 cm) was first immersed in a mixed solution of 2.5 M NaOH and 0.125 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ for 20 min to achieve blue $\text{Cu}(\text{OH})_2$ precipitates on CF surface. The piece was washed with deionized water and ethanol for several times and dried in an air oven of 60 °C for 4 h. Subsequently, the sample dehydrated at 180 °C for 1 h at a speed of 2 °C min⁻¹. The obtained CF based piece is associated with the precursor CuO nanowire on Cu foil (CuO NW/CF). The sample of each step was washed and dried to get dried pieces for the next step of use.

Synthesis of ZnCo LDH/CF: In a typical procedure, 0.291 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.148 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.093 g of NH_4F and 0.30 g of urea were dissolved in a mixed solution of 60 mL of H_2O and 40 mL of ethanol. After being stirred for half hour, the solution was aged for three days. Then the solution was transferred into a 20 mL of teflon-lined stainless steel autoclave. A piece of CF was immersed into the reaction solution. The autoclave was sealed and heated to and maintained at 120 °C for 4 h in an electronic oven, and then cooled to room temperature naturally. After washed with distilled water and acetone repeatedly to obtain ZnCo LDH/CF.

Synthesis of hierarchical core-shell CuO@ZnCo LDH/CF: This hierarchical core-

shell CuO@ ZnCo LDH/CF was synthesized through a one-step hydrothermal method. All chemicals were analytical grade and used as received without further purification. In a typical procedure, 0.291 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.148 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.093 g of NH_4F and 0.30 g of urea were dissolved in a mixed solution of 60 mL of H_2O and 40 mL of ethanol. After being stirred for half hour, the solution was aged for three days. Then the solution was transferred into a 20 mL of teflon-lined stainless steel autoclave. A piece of CuO NW/CF was immersed into the reaction solution. The autoclave was sealed and heated to and maintained at 120 °C for 4 h in an electronic oven, and then cooled to room temperature naturally. After washed with distilled water and acetone repeatedly to obtain hierarchical core-shell CuO@ZnCo LDH/CF.

Synthesis of RuO_2 /CF: RuO_2 was prepared according to the previous report.¹ Briefly, 2.61 g of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and 1.0 mL NaOH (1.0 M) were added into 100 mL distilled water and stirred for 45 min at 100 °C. Then the solution was centrifuged for 10 minutes and filtered. The precipitate was collected and washed with water several times. Finally, the product was dried at 80 °C overnight and then annealed at 300 °C in air for 3 h. 20 mg RuO_2 and 10 μL 5 wt% Nafion solution were dispersed in 990 μL water/ethanol (V:V = 1:1) by 30 min sonication to form a catalyst ink. Then 45 μL catalyst ink was loaded on Cu foil with a loading mass of 10 mg cm^{-2} .

Characterizations: X-ray diffraction (XRD) analysis was performed using a LabX XRD-6100 X-ray diffractometer with Cu $\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 40 mA. Scanning electron microscope (SEM) measurements were recorded on a Gemini 300 at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (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 CHI660E potentiostat (CH Instruments, China) in a standard three-electrode setup, with the use of CuO@ZnCo LDH/CF as the working electrode, a graphite rod as the

counter electrode and Hg/HgO as the reference electrode. The potentials reported in this work were calibrated to RHE, using the following equation: $E \text{ (RHE)} = E \text{ (Hg/HgO)} + (0.098 + 0.059 \text{ pH}) \text{ V}$. Polarization curves were obtained by linear sweep voltammetry with a scan rate of 2 mV s^{-1} .

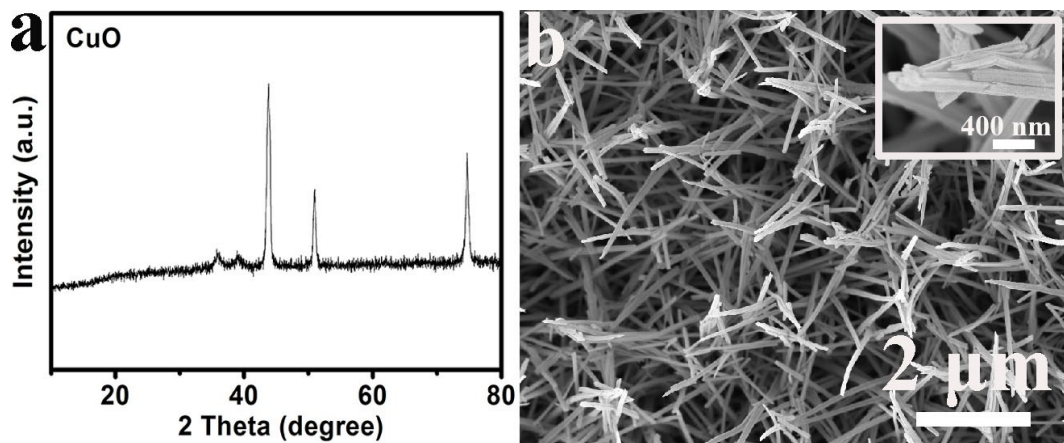


Fig. S1. (a) XRD pattern for CuO NW/CF. (b) SEM images for CuO NW/CF.

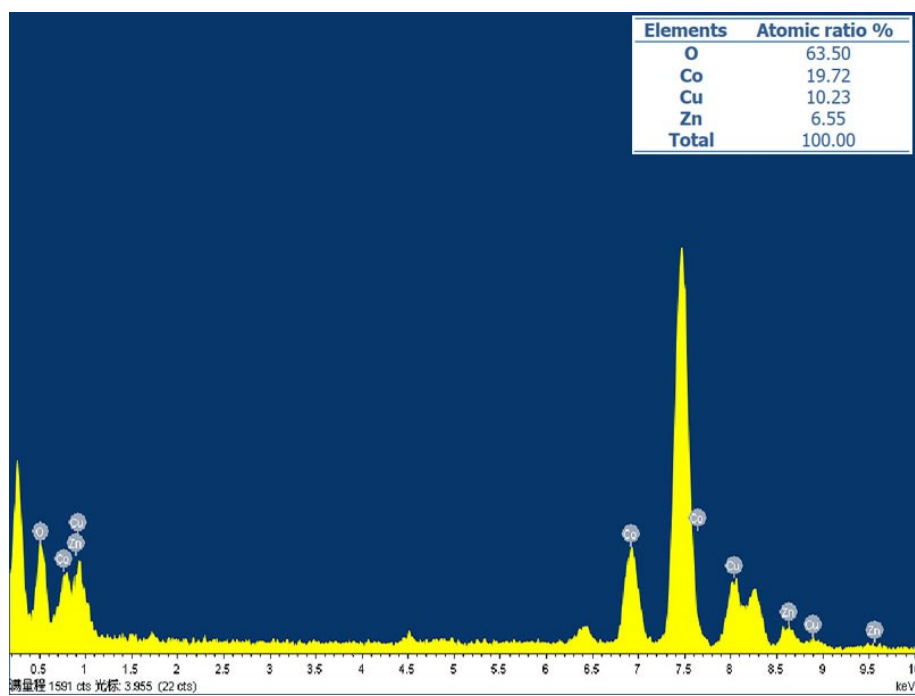


Fig. S2. EDX spectrum of CuO@ZnCo LDH/CF.

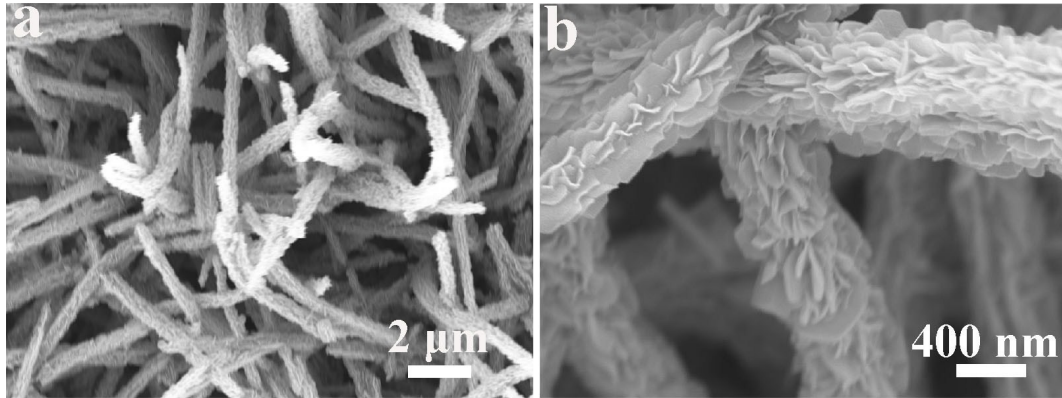


Fig. S3. SEM images for CuO@ZnCo LDH/CF after stability test.

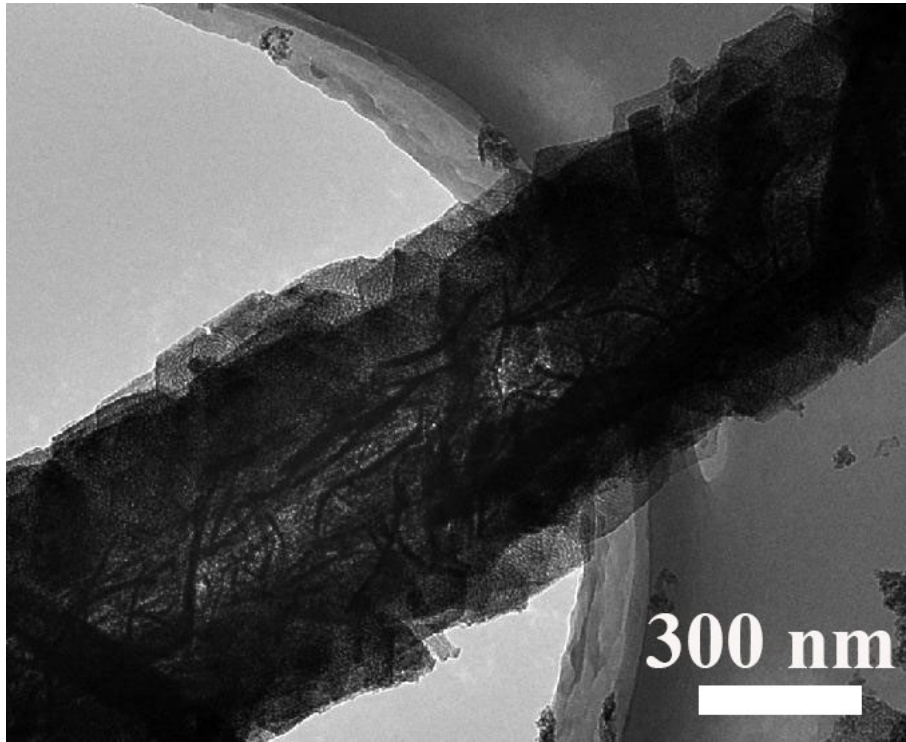


Fig. S4. TEM image for CuO@ZnCo LDH after stability test.

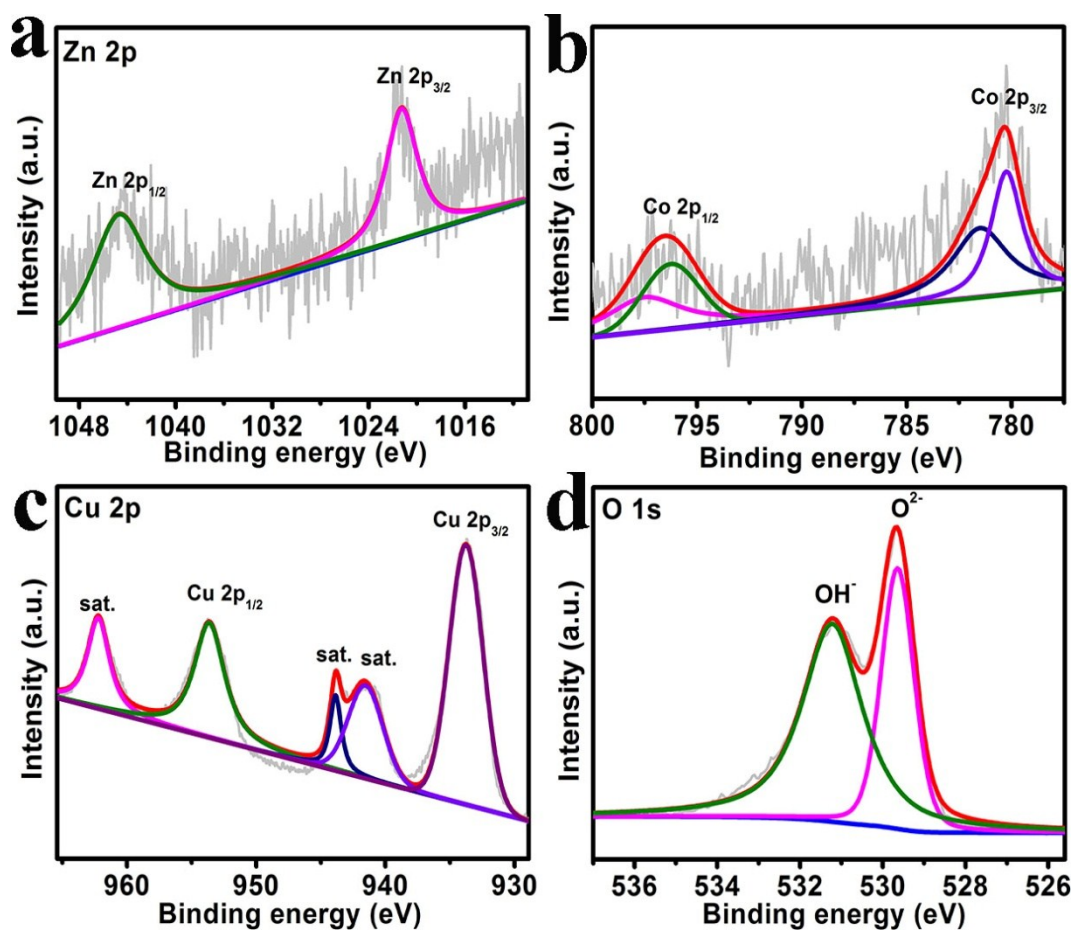


Fig. S5. XPS spectra of CuO@ZnCo LDH/CF in the (a) Zn 2p, (b) Co 2p, (c) Cu 2p, and (d) O 1s regions after stability test.

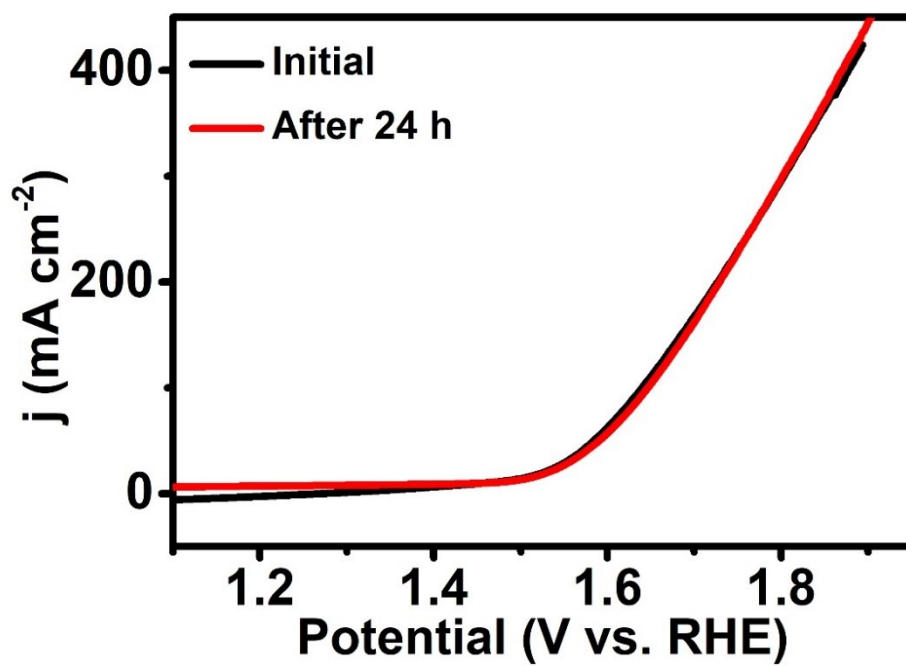


Fig. S6. LSV curves for CuO@ZnCo LDH/CF before and after stability tests.

Table S1. Comparison of CuO@ZnCo LDH/CF and other non-noble-metal catalysts for OER performance in alkaline media.

Catalyst	Electrolyte	j (mA cm ⁻²)	Overpotential (mV)	Ref.
CuO@ZnCo LDH/CF	1.0 M KOH	10	270	This work
ZnCo LDH/rGO	1.0 M KOH	10	330	2
ZnCo LDH/NF	1.0 M KOH	2	330	3
ZnCo LDH	1.0 M KOH	10	375	4
Cu/(Cu(OH) ₂ -CuO)	1.0 M KOH	10	350	5
Zn _x Co _{3-x} O ₄	1.0 M KOH	10	320	6
CCH/C	0.1 M KOH	10	509	7
CuCoO-NWs	1.0 M KOH	10	380	8
Cu(OH) ₂ @CoCO ₃ (OH) ₂ ·nH ₂ O	1.0 M KOH	50	270	9
Cu(OH) ₂ @NiFe LDH	1.0 M KOH	10	283	10
Cu@NiFe LDH/CF	1.0 M KOH	10	310	11
NiCo LDH	1.0 M KOH	10	367	12
CoO _x @CN	1.0 M KOH	10	370	13
Cu@CoS _x /CF	1.0 M KOH	10	160	14
Co@Co ₃ O ₄ /NC-1	0.1 M KOH	10	420	15

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