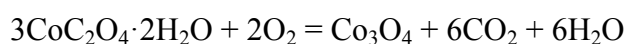
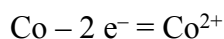


Electronic Supplementary Information

Experimental section

Materials: Pure Co foil (>99.95%, Sigma-Aldrich) was used as a starting substance for the fabrication of cobalt complexes. H₂C₂O₄ were purchased from Aladdin Ltd. in Shanghai. Acetone and ethanol were purchased from Tianjin Chemical Corporation. RuCl₃·3H₂O and Nafion (5 wt%) were bought from Sigma-Aldrich Chemical Reagent Co., Ltd. All chemical reagents were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Preparation of Co₃O₄ NA/CF: CoC₂O₄·2H₂O NA/CF was prepared as follows. In a typical synthesis, a piece of Co foil (1 cm × 2 cm, thickness: 0.5 mm) was well cleaned by sonication sequentially in acetone, water and ethanol for 10 min each before use, and was immediately dried in the oven at 50 °C for 5 min. CoC₂O₄·2H₂O NA/CF were electrodeposited in (0.05 M, 50 mL) H₂C₂O₄ solution, with potential of 1.0 V for 150 min at 25 °C. The CoC₂O₄·2H₂O array was converted to Co₃O₄ by thermal decomposition under Ar conditions at 400 °C for 2 h. The weight increment (x mg) of Co foil can be directly weighted after the growth of Co₃O₄. Co₃O₄ loading = x mg (M_{Co₃O₄}/M_O) = x mg (240/16) = 15x mg, where M is the molecular weight or atomic weight. For Co₃O₄ NA/CF electrode, the loading mass of Co₃O₄ is about 1.9 mg cm⁻². To investigate the formation processes, morphology changes and electrocatalytic performance for CoC₂O₄·2H₂O NA/CF, different reaction times (10, 70, and 150 min) and potentials (0.5 and 1.0 V) were used while keeping other parameters unchanged. These redox reactions may be:



Synthesis of Co₃O₄ sheets: 1 g of Co(CH₃COO)₂·4H₂O, and 0.05 g of PVP (M_w = 30000 g/mol) were loaded into a 100 mL poly(tetrafluoroethylene) (PTFE)-lined stainless steel autoclave, which was then filled with 80 mL mixture solution of ethylene glycol and water. The autoclave was sealed and maintained at 180 °C for 12

h, and then cooled down to room temperature. The final products were centrifuged, rinsed with distilled water and ethanol several times to remove any impurities. The as-prepared precursors were finally calcined at 350 °C in N₂ for 3 h.

Synthesis of Co₃O₄ spheres: 1 g of Co(CH₃COO)₂·4H₂O and 0.05 g of PVP (M_w = 30000 g/mol) were loaded into a 100 mL poly(tetrafluoroethylene) (PTFE)-lined stainless steel autoclave, which was then filled with 80 mL ethylene glycol. The autoclave was sealed and maintained at 180 °C for 12 h, and then cooled down to room temperature. The final products were centrifuged, rinsed with distilled water and ethanol several times to remove any impurities. The as-prepared precursors were finally calcined at 350 °C in N₂ for 3 h.

Synthesis of RuO₂: RuO₂ was prepared in accordance with reported work.¹ Briefly, 2.61 g of RuCl₃·3H₂O and 1.0 mL KOH (1.0 M) were added into 100 mL distilled water and stirred for 45 min at 100 °C. Then the above solution was centrifuged for 10 minutes and filtered. The precipitates were collected by centrifugation and washed with water for several times, followed by drying at 70 °C. Finally, the product was annealed at 300 °C for 3 h under air atmosphere. RuO₂ ink was prepared by dispersing 20 mg of catalyst into 490 μL of water/ethanol (v/v = 1:1) and 10 μL of 5 wt% Nafion using sonication for 30 min. Then 11.3 μL of the RuO₂ ink (containing 452 μg of RuO₂) was loaded onto a bare Co foil of 0.25 cm² in geometric area (loading: 1.9 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 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 collected 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. Brunauer-Emmett-Teller (BET) measurements were performed by using N₂ absorption method with a

Micromeritics Tristar II 3020 instrument at 77 K. All the samples were degassed at 150 °C under vacuum for over 6 h.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system. Co₃O₄ NA/CF foil was used as the working electrode. A graphite plate and Hg/HgO were used as the counter electrode and the reference electrode, respectively. The temperature of solution was kept at 25 °C for all the measurements via the adjustment of air condition and heating support, which ensured the variation of diffusion coefficient below 1%. The potentials reported in this work were calibrated to RHE other than especially explained, using the following equation: $E(\text{RHE}) = E(\text{Hg/HgO}) + (0.098 + 0.059 \text{ pH}) \text{ V}$. Electrochemical preparation curves were obtained by amperometric i-t curve with a scan rate of 100 mV s⁻¹.

Tafel plots calculation: The Tafel plots are employed to evaluate the OER catalytic kinetics and fitted with the following equation (1):

$$\eta = b \log j + a \quad (1)$$

Where j is the current density and b is the Tafel slope.

TOF calculation: The TOF is quantified the concentration of active site and calculates by the equation (2):

$$\text{TOF} = jA/4Fm \quad (2)$$

Where j is current density (A cm⁻²) at defined overpotential; A is the geometric area of the testing electrode; 4 indicates the mole of electrons consumed for evolving one mole O₂ from water; F is the Faradic constant (96485 C mol⁻¹); m is the number of active sites (mol), which can be extracted from the linear relationship between the oxidation peak currents and scan rates by the equation (3):

$$\text{slope} = n^2F^2m/4RT \quad (3)$$

Where n is the numbers of electron transferred; R and T are the ideal gas constant and the absolute temperature, respectively.

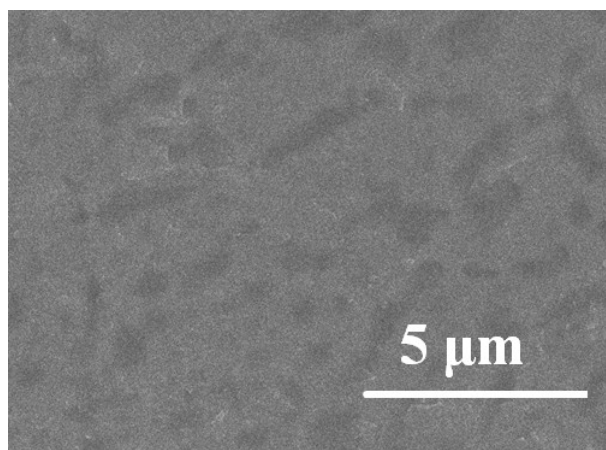


Fig. S1. SEM image of bare Co foil.

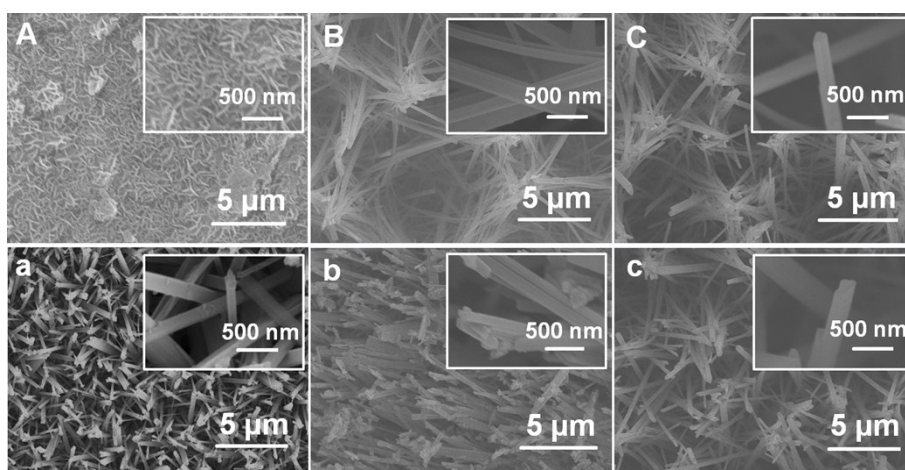


Fig. S2. SEM images of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ NA/CF with different electrodeposited condition in 0.05 M $\text{H}_2\text{C}_2\text{O}_4$ solution: 10 min (A and a), 70 min (B and b), 150 min (C and c), 0.5 V (A, B and C), 1.0 V (a, b and c).

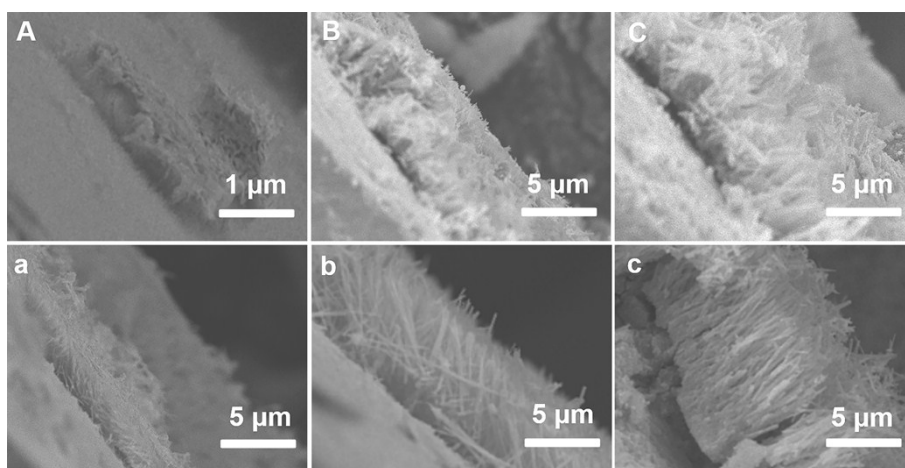


Fig. S3. Side-viewed SEM images of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ NA/CF with different electrodeposited condition in 0.05 M $\text{H}_2\text{C}_2\text{O}_4$ solution: 10 min (A and a), 70 min (B and b), 150 min (C and c), 0.5 V (A, B and C), 1.0 V (a, b and c).

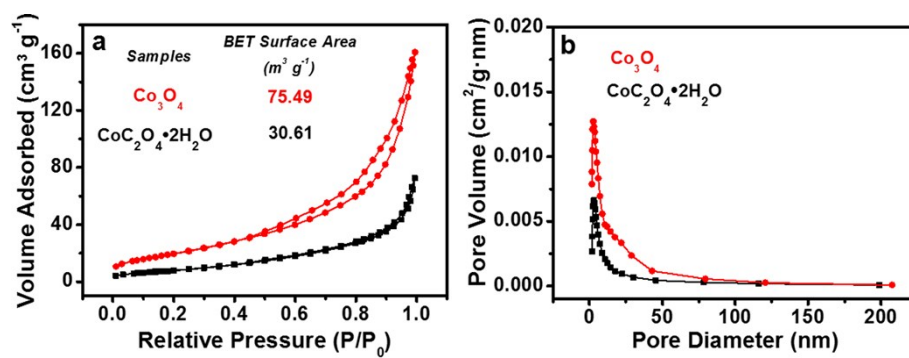


Fig. S4. Nitrogen adsorption-desorption isotherms (a) and the corresponding pore size distribution (b).

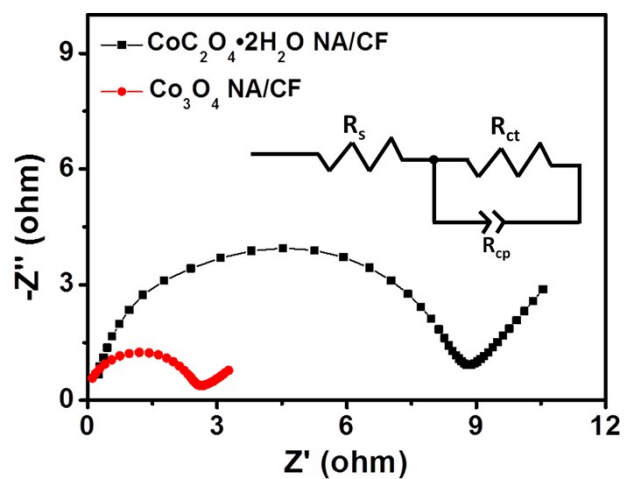


Fig. S5. Nyquist plots for $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ NA/CF and Co_3O_4 NA/CF in the frequency range from 0.01 to 10^6 Hz at open circuit potential (0.251 V vs. Hg/HgO) in 1.0 M KOH.

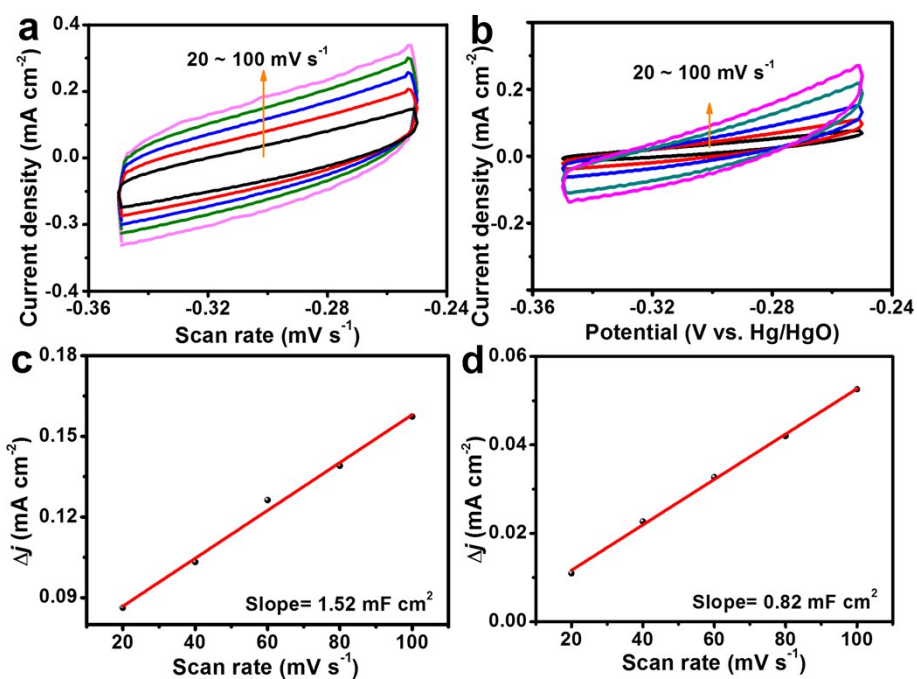


Fig. S6. CVs for (a) Co₃O₄ NA/CF and (b) CoC₂O₄·2H₂O NA/CF in the non-faradaic capacitance current range at scan rates of 20, 40, 60, 80, and 100 mV s⁻¹. Corresponding capacitive currents at -0.30 V vs. Hg/HgO as a function of scan rates for (c) Co₃O₄ NA/CF and (d) CoC₂O₄·2H₂O NA/CF.

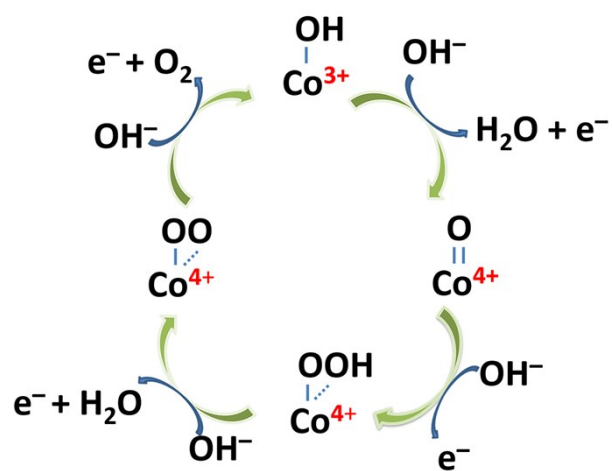


Fig. S7. Scheme of the proposed OER mechanism on Co_3O_4 .

Table S1. Comparison of OER performance for Co₃O₄ NA/CF with other Co-based WOCs in alkaline media.

Catalyst	j (mA cm ⁻²)	η (mV)	Electrolyte	Ref.
Co ₃ O ₄ NA/CF	15	308	1.0 M KOH	This work
	50	343		
	15	347	0.1 M KOH	
	50	379		
Co ₃ O ₄ nanocrystal /carbon paper	50	420	1.0 M KOH	2
Co@Co ₃ O ₄ /NC	25	~390	0.1 M KOH	3
CoO _x NPs/BNG	25	~340	0.1 M KOH	4
Co-CNT/PC	25	~390	0.1 M KOH	5
Co ₃ O ₄ C-NA	25	~350	0.1 M KOH	6
Co ₃ O ₄ /NiCo ₂ O ₄	50	~418	1.0 M KOH	7
Co ₃ O ₄	25	~326	1.0 M KOH	8
Co ₃ O ₄ -MTA	150	360	1.0 M KOH	9
Co ₃ O ₄ /MNTs	25	~373	1.0 M KOH	10
Co-P films	25	365	1.0 M KOH	11
Co-S nanosheets	50	410	1.0 M KOH	12
NiCo ₂ S ₄ nanowires	100	340	1.0 M KOH	13
NiCo LDH	50	440	1.0 M KOH	14
Hierarchical Zn _x Co _{3-x} O ₄	50	400	1.0 M KOH	15
Au@Co ₃ O ₄ Core-Shell	25	370	0.1 M KOH	16
Cobalt carbonate hydroxide	30	720	0.1 M KOH	17
Co ₃ O ₄ /carbon porous nanowire	50	390	0.1 M KOH	18
Cobalt carbonate hydroxide/MWCNT	50	353	0.1 M KOH	19
CeO ₂ /CoSe ₂	30	338	0.1 M KOH	20
Cu _x Co _{3-x} O ₄ nanoparticles	100	367	1.0 M KOH	21
Co ₃ O ₄ nanoparticles	50	510	0.1 M KOH	22
mesoporous Co ₃ O ₄	100	525	1.0 M KOH	23
graphene-CoO nanohybrids	15	430	0.1 M KOH	24
NiCo ₂ S ₄ @graphene	30	470	1.0 M KOH	25
Mn ₃ O ₄ /CoSe ₂	50	450	1.0 M KOH	26

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