

Supplementary Information

Interfacial Electron Redistribution in CoS₂/Co₃O₄ Heterostructures Enabled by *In-Situ* Anion-Driven Topochemical Transformation toward Efficient Oxygen Evolution

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Dedication

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Experimental section

Chemicals

Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), polyvinylpyrrolidone (PVP), 2-methylimidazole (MeIM), Triethylamine (TEA) were purchased from Aladdin Biochemical Technology Co., Ltd. Polyacrylonitrile (PAN) was purchased from Macklin Biochemical Co., Ltd. Methanol, potassium hydroxide (KOH) and N, N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. Nafion was purchased from Sigma-Aldrich. Pt/C (20 wt.%) was purchased from Johnson Matthey Chemicals Co., Ltd. All chemicals were used as received without further purification.

Synthesis of ZIF-67

ZIF-67 cubes were prepared based on the previously reported method with modifications.^[1] 4.74 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 4.00 g PVP were dissolved in 400 mL methanol as solution A. Solution B was formed by dissolving 5.30 g MeIM and 400 μL TEA in another 400 mL methanol. Then, solution A was rapidly injected into solution B with continuous stirring at room temperature. After stirring well, the solution was left at room temperature for 24 h. The precipitates were collected by centrifugation and washed three times with methanol. Finally, the products were dried under vacuum at 60 °C for 24 h (denoted as ZIF-67, **Figure S1**).

Materials characterization

X-ray diffraction (XRD) patterns were characterized by Rigaku D/max-RC diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm). Scanning electron microscopy (SEM) images and energy-dispersive spectroscopy (EDS) were collected using a Hitachi S5500 scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were carried out at a JEOL JEM-2010F transmission electron microscope. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo VG Scientific ESCALAB 250 spectrometer with an Al $K\alpha$ light source to characterize the compositions and valence states of the products. Raman spectra were conducted on a Raman spectrometer (Lab RAM HR800, $\lambda = 514$ nm). Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) measurements were performed using an Agilent 730 ICP-OES instrument. UPS measurements were performed on a Thermo Scientific ESCALAB 250 X I system using a He I ultraviolet source with a photon energy of 21.22 eV. A sample bias of -5 V was applied

during the measurement to obtain the secondary-electron cutoff. The work function was calculated from the secondary-electron cutoff according to $\Phi = h\nu - E_{\text{cutoff}} - E_F$.

Electrochemical measurement

All electrochemical measurements of the OER were performed on a CHI 760E workstation with a three-electrode system equipped with a Pine high-speed rotator. A typical three-electrode structure uses a graphite rod as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and a glassy carbon electrode (GCE) as the working electrode. To prepare the catalyst ink, 5 mg of the as-synthesized catalyst powder were dispersed into 1 mL of ethanol solution (the volume ratio of ethanol to water was 1:3) for at least 30 min under ultrasonication. Then, 8 μL of the obtained ink was dropped on the surface of polished GCE and then dried at 40 $^{\circ}\text{C}$. Subsequently, 4 μL of Nafion (5 wt.%, Sigma-Aldrich) was dropped on the surface of catalysts modified GCE and then dried before electrochemical test. The OER test was performed by linear sweep voltammetry (LSV) in N_2 -saturated 1.0 M KOH solution at a scan rate of 5 mV s^{-1} . The electrochemical electric double layer capacitance (C_{dl}) was determined from a series of CV curves recorded by cyclic voltammetry in the non-Faraday region at various scan rates ranging from 20 to 100 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) was measured at an open-circuit voltage with an amplitude of 10 mV in the frequency range of 0.01 Hz-100 kHz. The stability of the catalyst was tested at a constant voltage (0.52 V). In this work, all potentials were calculated using a reversible hydrogen electrode (RHE) as a standard. The calculation formula is as follows: $E_{\text{RHE}} = E_{\text{SCE}} + 0.0592 \text{ pH} + 0.242$. The apparent Turnover frequency (TOF) for OER was calculated at 1.63 V vs. RHE according to $\text{TOF} = I / (4Fn_{\text{Co}})$, where I is the current at 1.63 V vs RHE, F is the Faraday constant (96485 C mol^{-1}), and n_{Co} is the molar amount of Co determined by ICP-OES. All Co atoms were conservatively assumed to be catalytically accessible sites.

Zn-air battery Measurements

The laborator-constructed portable rechargeable Zn-air batteries (ZABs) was assembled from three parts: an anode, an electrolyte, and a cathode. The anode was a polished zinc plate with a thickness of 0.3 mm. The electrolyte was an aqueous solution composed of 0.2 M ZnCl_2 +6M KOH. The air cathode was composed of hydrophobic carbon paper coated with

catalyst (2 mg cm^{-2}) and nickel foam. The effective contact area between the air cathode and electrolyte was 1 cm^2 . Where, the side coated with catalyst faces the liquid layer, and the side uncoated with catalyst faces the gas diffusion layer, so that O_2 diffuses from the atmosphere into the catalyst. The ZAB fittings were assembled sequentially and placed for 1 hour before testing. The cycle test was performed using the Land CT2001A system at 5 mA cm^{-2} per discharge and charge. Each discharge and charge cycle was set to 20 min.

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Figures and Table

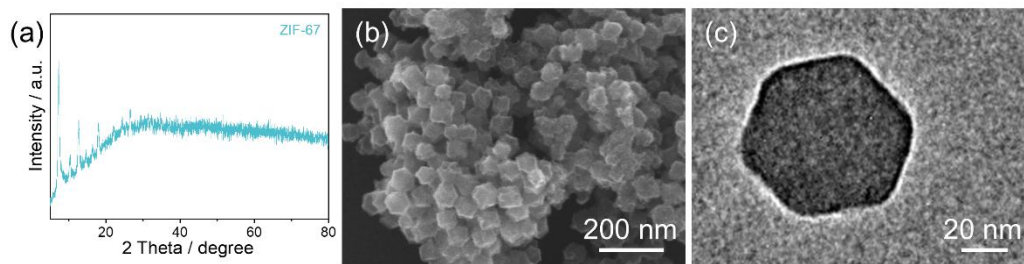


Figure S1. (a) XRD pattern, (b) SEM and (c) TEM images of the ZIF-67.

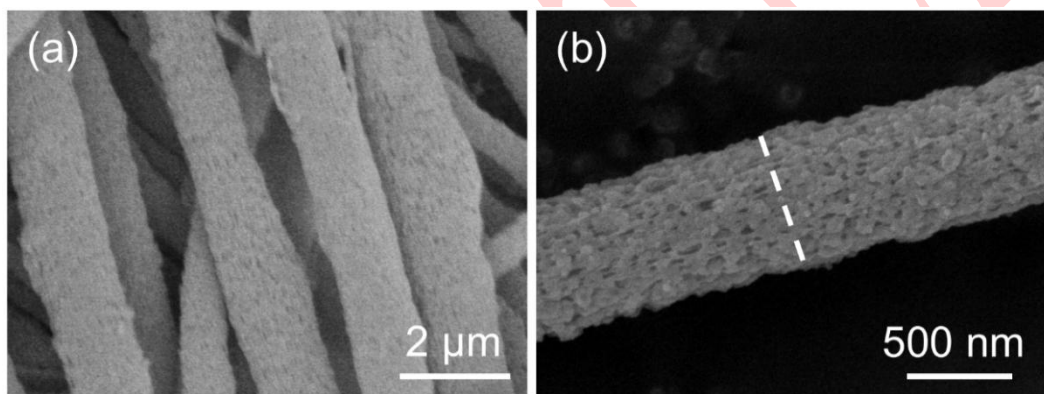


Figure S2. (a)-(b) SEM images of the Co^{2+} -[2-MeIm]@NFs.

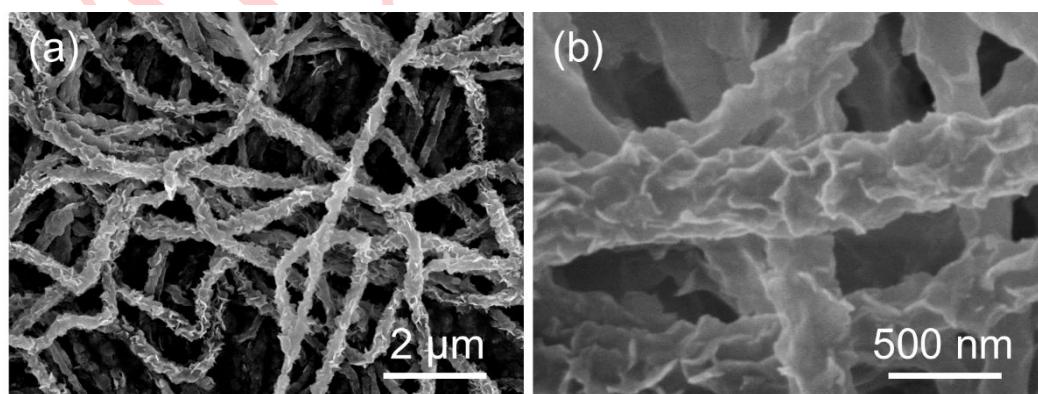


Figure S3. (a)-(b) SEM images of the Co(OH)_2 @NFs.

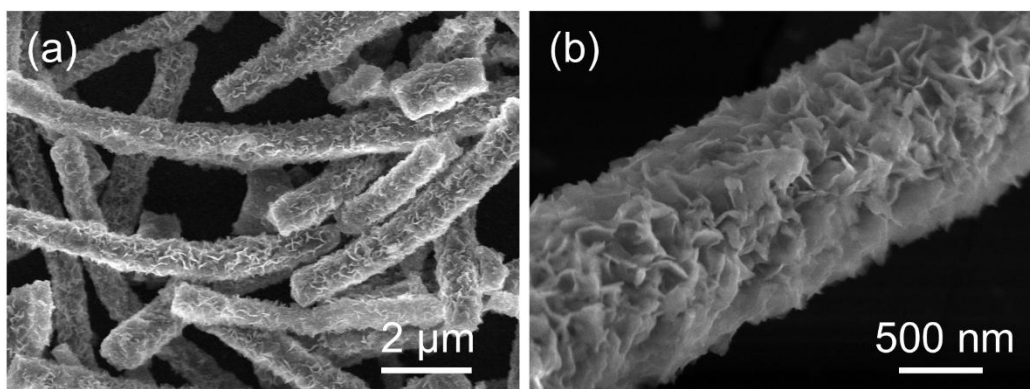


Figure S4. (a)-(b) SEM images of the $\text{Co}_3\text{O}_4@\text{CFs}$.

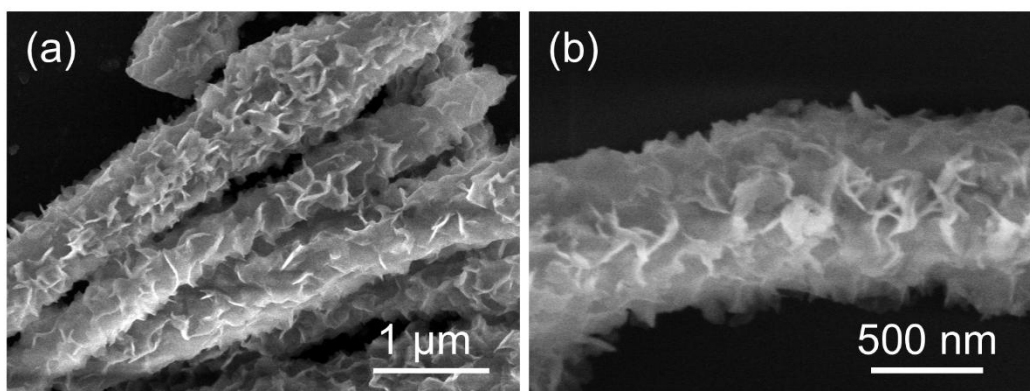


Figure S5. (a)-(b) SEM images of the $\text{CoS}_2@\text{CFs}$.

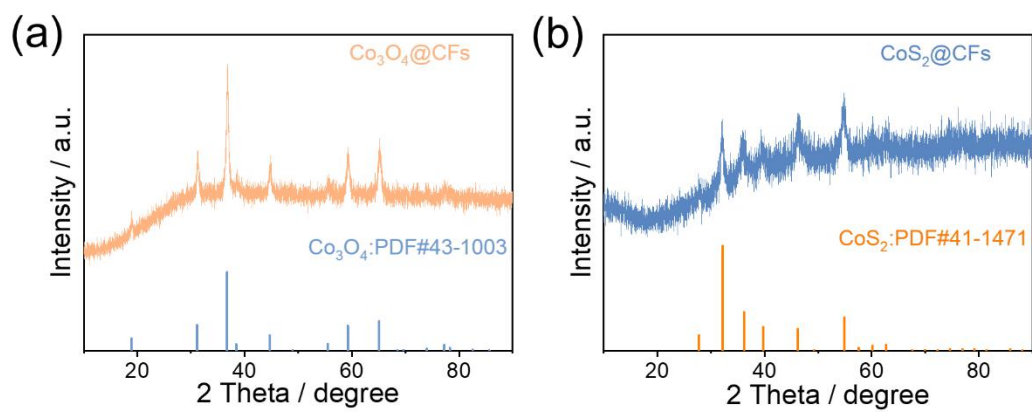


Figure S6. (a)-(b) XRD patterns of the $\text{Co}_3\text{O}_4@\text{CFs}$ and the $\text{CoS}_2@\text{CFs}$.

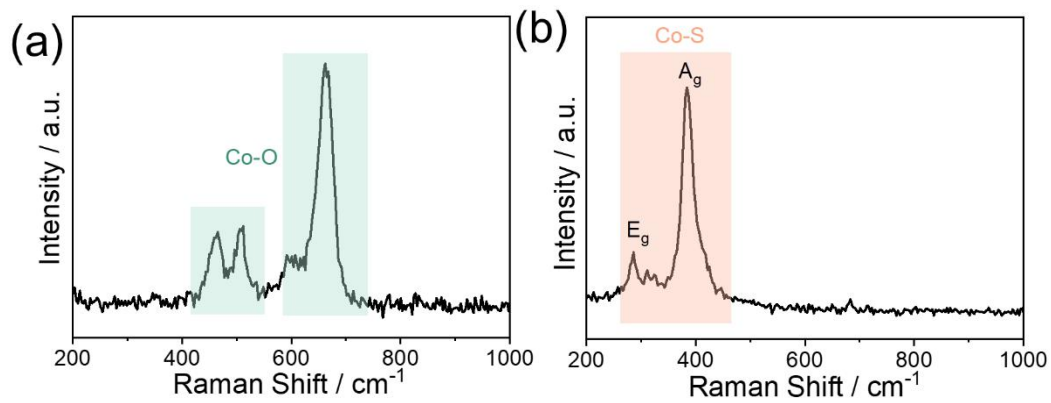


Figure S7. (a)-(b) Raman spectrums of the $\text{Co}_3\text{O}_4@\text{CFs}$ and the $\text{CoS}_2@\text{CFs}$.

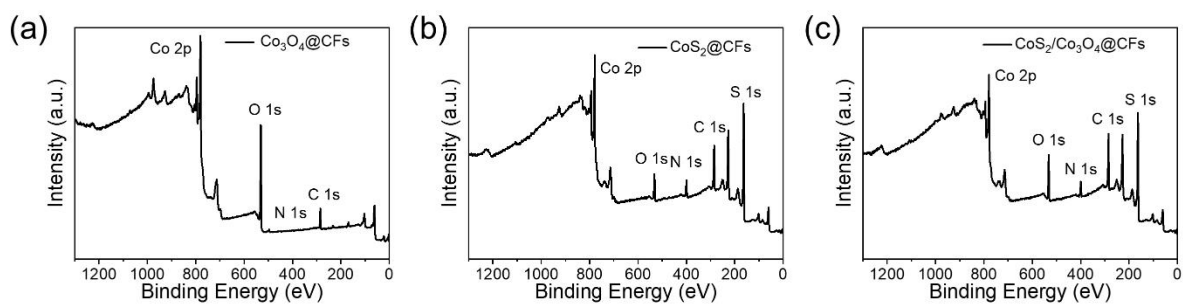


Figure S8. XPS survey spectra of: (a) the $\text{Co}_3\text{O}_4@\text{CFs}$, (b) the $\text{CoS}_2@\text{CFs}$, and (c) the $\text{CoS}_2/\text{Co}_3\text{O}_4@\text{CFs}$.

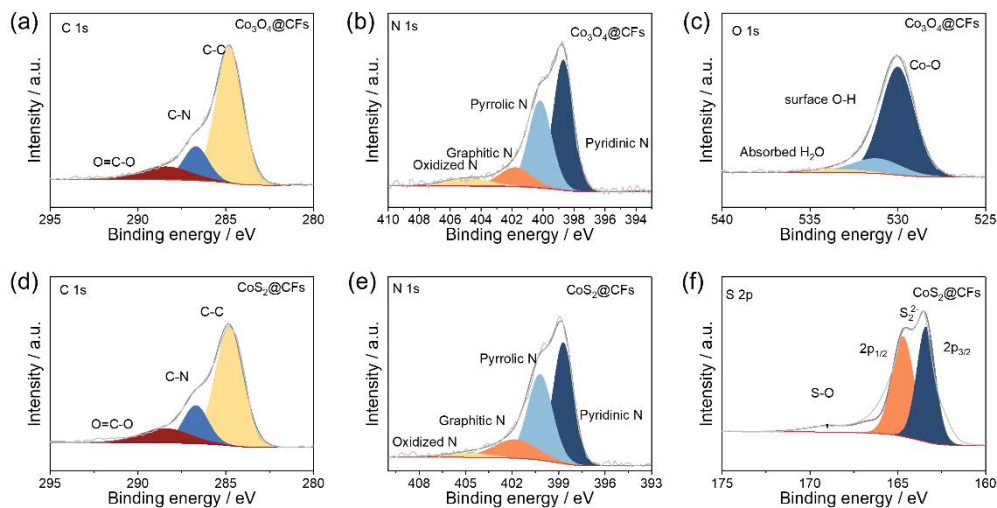


Figure S9. The high-resolution XPS spectra: (a) C 1s, (b) N 1s, (c) O 1s of $\text{Co}_3\text{O}_4@\text{CFs}$, and (d) C 1s, (e) N 1s, (f) S 2p of $\text{CoS}_2@\text{CFs}$.

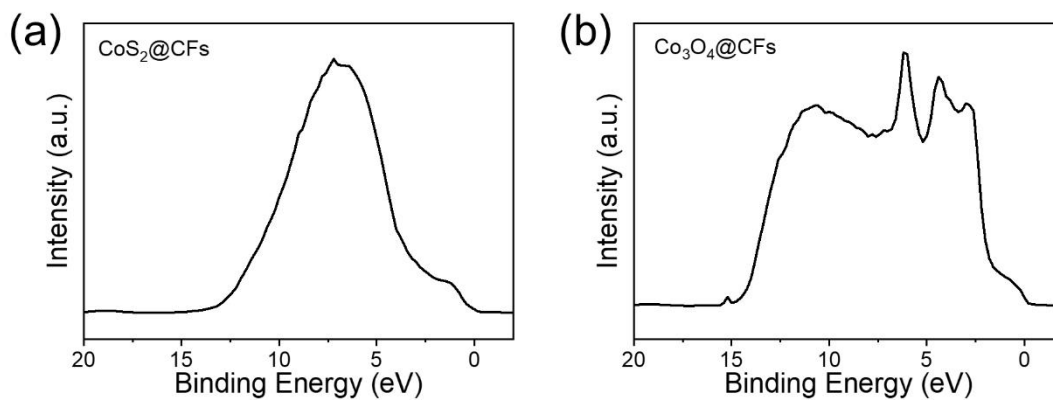


Figure S10. UPS survey spectra of: (a) the $\text{CoS}_2@\text{CFs}$, and (b) the $\text{Co}_3\text{O}_4@\text{CFs}$.

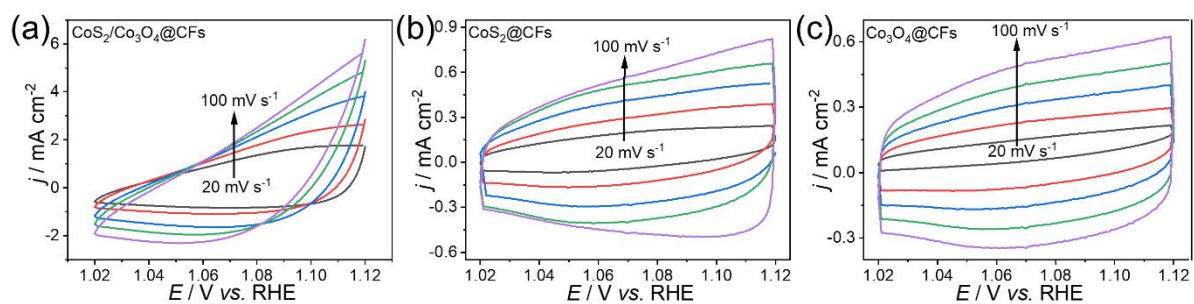


Figure S11. CV curves of: (a) $\text{CoS}_2/\text{Co}_3\text{O}_4@\text{CFs}$, (b) $\text{Co}_3\text{O}_4@\text{CFs}$ and (c) $\text{CoS}_2@\text{CFs}$ at different scanning rates from 20 to 100 mV s⁻¹.

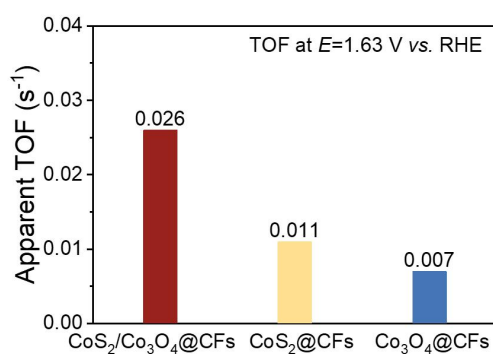


Figure S12. The apparent TOF of $\text{CoS}_2/\text{Co}_3\text{O}_4@\text{CFs}$, $\text{CoS}_2@\text{CFs}$, and $\text{Co}_3\text{O}_4@\text{CFs}$.

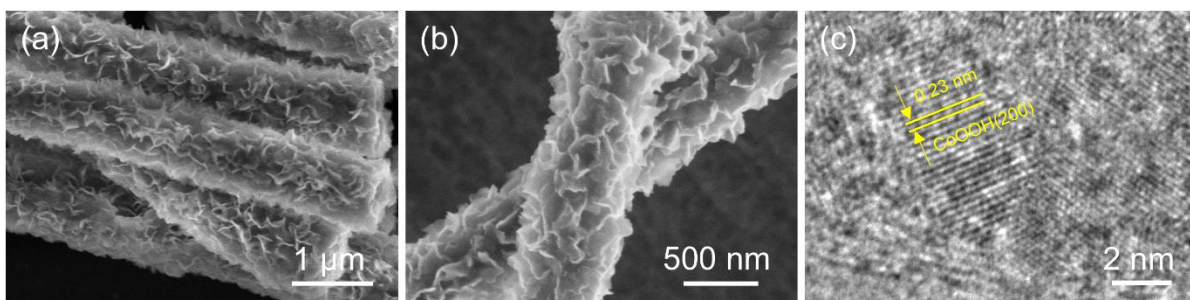


Figure S13. (a)-(b) SEM, and (c) HRTEM images of $\text{CoS}_2/\text{Co}_3\text{O}_4@\text{CFs}$ after the stability test.

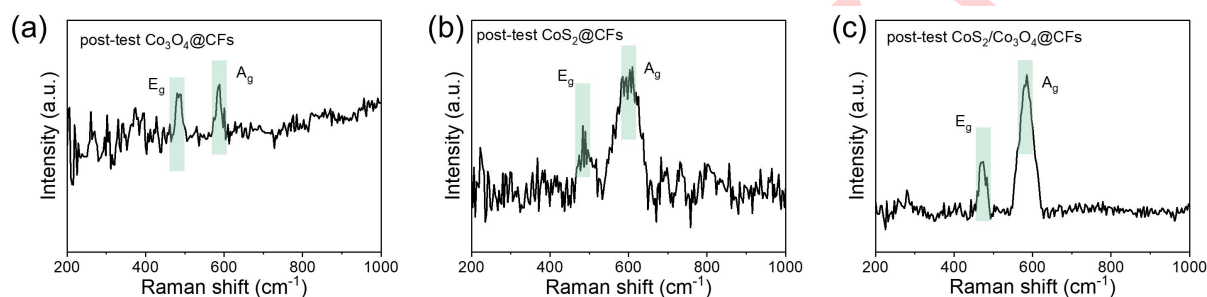


Figure S14. Raman spectra after the stability test of: (a) $\text{Co}_3\text{O}_4@\text{CFs}$, (b) $\text{CoS}_2@\text{CFs}$, and (c) $\text{CoS}_2/\text{Co}_3\text{O}_4@\text{CFs}$.

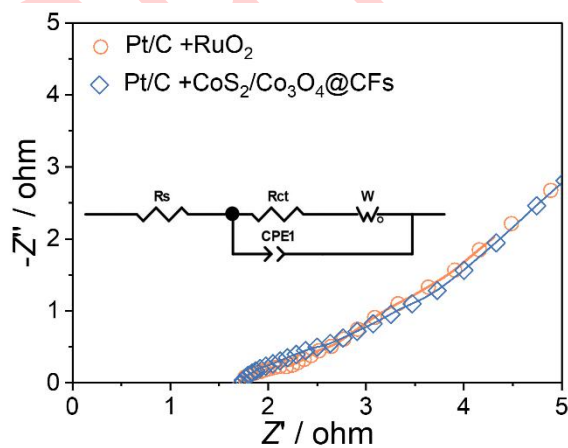


Figure S15. The EIS analysis result of $\text{CoS}_2/\text{Co}_3\text{O}_4@\text{CFs}+\text{Pt/C}$ - and $\text{RuO}_2+\text{Pt/C}$ -based ZABs at the open-circuit potential.

Table S1. Comparison of OER performance of CoS₂/Co₃O₄@NCNFs with some previously reported nonprecious OER catalysts in 1.0 M KOH solution.

Catalyst	Overpotential / mV (10 mA cm ⁻²)	Tafel slop (mV dec ⁻¹)	Reference
CoS ₂ /Co ₃ O ₄ @CFs	304	69.9	This work
FeCo/Co ₂ P@NPCF	330	61	[2]
Co/Co _x M _y	334	79.2	[3]
Ce-MnCo ₂ O ₄	390	125	[4]
H-CoTe ₂ /NiTe ₂ @NCBs	320	64.8	[5]
Co-N/GF-700	313	84.1	[6]
NiO/NiCo ₂ O ₄	357	130	[7]
CoSe ₂ @NC	340	72.4	[8]
ZnCo ₂ O ₄	350	24	[9]
CoP@PNC-DoS	316	42.9	[10]
Co ₂ P/CoNPC	326	72.6	[11]
FeCu/FeF ₃ @HPCNFs	377	74	[12]
Fe@BIF-91	350	71	[13]
Co/Co ₃ O ₄ @PGS	350	76.12	[14]
NiCo@NiCoO ₂ /C	366	83.97	[15]

Table S2. The element content obtained through ICP testing.

Catalyst	Co (wt.%)
CoS ₂ @CFs	53.9
CoS ₂ /Co ₃ O ₄ @CFs	54.6
Co ₃ O ₄ @CFs	59.7

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