Bimetallic-organic framework-derived Co-ZnO grown on carbon nanofibers as bifunctional electrocatalysis for rechargeable Zn-air batteries

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1. Materials

Polyacrylonitrile (PAN, M_w = 80 000), N, N-dimethyformamide (DMF, 98 %), potassium hydroxide (KOH, ≥85%), methanol (99.5%), zinc acetate ($Zn(OAc)_2$, 99%), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 99%) and 2-methylimidazole (2-MI, 98%) were directly used without further purification. Carbon black and commercial Pt/C were obtained from Shanghai Hesen Electric Co. Ltd. Ruthenium oxide (RuO_2) was chased from Aladdin. Deionized water was used for all the catalyst synthesis and electrochemical tests.

2. Physicochemical characterizations

The nanostructure of 2-MI/PAN, Co-Zn-ZIF/PAN, Co-ZIF/PAN, Co-Zn/CNFs and Co/CNFs were explored by scanning electron microscopy (SEM, Pro, Phenom, Netherlands). The lattice fringes and interfacial structures of nanomaterials were characterized by transmission electron microscopy (TEM, JEM-2100 JEOL, Japan). X-ray diffraction (XRD, Rigaku Ultima IV, Japan) analysis was conducted with a Cu Kα (λ = 0.15406 nm) radiation source. The specific surface area and pore size distribution were determined using a Quanta chrome instrument (ASIQM-0001-3 instrument, USA). X ray photoelectron spectroscopy (XPS, Escalab 250 xi. Thermo Fisher Scientific USA) was carried out on Al Kα radiation source. The Raman spectroscopya (InVia Microscope Raman, Renishaw, England) was conducted on an argon laser source. Thermogravimetric analysis (TGA) was performed using STA-449F3 (NETZSCH Instruments, German). Temperature increases at 5 ℃/min under nitrogen atmosphere.

3. Electrochemical measurements

All OER/ORR tests are performed using a three-electrode system.

OER: Catalyst ink was prepared by adding deionized water (100 μL), ethanol (98 μL) and Nafion solution (2 μL) to catalyst sample (1 mg). Drops were placed on carbon paper at a loading of 1.5 mg/cm^2. Oxygen (99.9%) was filled into a four-mouth bottle containing 1.0 M KOH for 30 min before the test, followed by 50 cycles of cyclic voltammetry activation.

ORR: Catalyst ink was prepared in the same way as for OER. The catalyst ink (15 μL) was loaded onto a GC electrode (0.195 mg/cm^2). Cyclic voltammetry (CV) studies were performed in nitrogen- and oxygen-saturated 0.10 M KOH solution at a scan rate of 100 mV s^{-1}.

The overpotential and electron transfer numbers were calculated using the following equations:

$$E_{RHE} = E_{SCE} + 0.0592\ pH + 0.241\ V$$

$$n = 4I_d / (I_d + I_r/N)$$

Which E_{RHE} is the potential vs. Reversible hydrogen electrode (RHE), E_{SCE} is the potential vs. calomel electrode, and pH is the pH value of electrode.

Double layer capacitors (C_{dl}) were tested at different CV scan speeds of 20, 40, 60, 80, 100, and 120 mV s^{-1}. The potentials were calculated by the formula:

$$E_{\mathrm{RHE}} = E_{\mathrm{Hg/HgO}} + 0.0592\ \mathrm{pH} + 0.098\ \mathrm{V}$$

Which E_{RHE} is the potential *vs.* Reversible hydrogen electrode (RHE), $E_{\mathrm{Hg/HgO}}$ is the potential vs. Hg/HgO electrode, and pH is the pH value of electrode.

The current density normalised by electrochemical active surface area was calculated using the following equation:

$$J_{\mathrm{ECSA}} = \frac{I}{C_{\mathrm{dl}}/C_S}$$

Where J_{ECSA} is the current density normalised by ECSA (mA cm^{-2}); I is the current (mA); C_{dl} is the double layer capacitance, Cs is the specific capacitance for a 1 cm^2 flat surface, which is generally considered as 0.040 mF cm^{-2} in alkaline solution.

Turnover frequency (TOF) values were calculated below:

$$\mathrm{TOF} = j \times S / (z \times F \times n_{metal})$$

S is the surface area coated by catalysts; j is the current density; z is the accepted or donated electrons for the generation of each H_2 or O_2 molecule (4 for OER/ORR process); F is the Faraday constant (96485.3 C mol^{-1}); n_{metal} represents the amount of moles of all the active metal.

The zinc-air battery consisted of zinc foil, 6.0 M KOH and 0.2 M $Zn(Ac)_2$ electrolyte, Whatman TM glass microfiber spacer and nickel foam. The catalyst was formulated 1:1 with carbon black to form an ink (water (100 μL), ethanol (98 μL) and Nafion solution (2 μL)) drop on carbon paper (loaded with 1.0 mg cm^{-2}). Pt/C+RuO_2 was loaded on carbon paper (1.0 mg cm^{-2}).

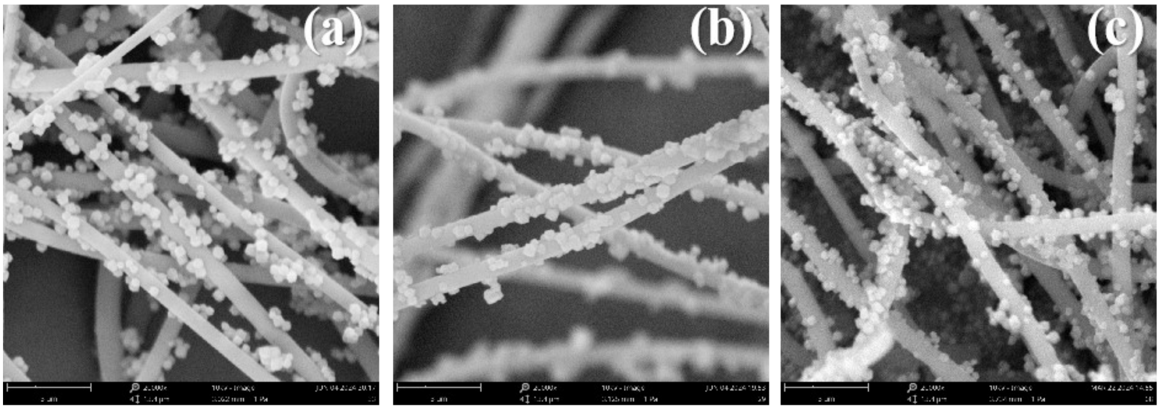

Fig. S1 (a), (b), (c) and (d) SEM images of the Co-Zn-ZIF/PAN-4, Co-Zn-ZIF/PAN-1 and Co-ZIF/PAN, respectively.

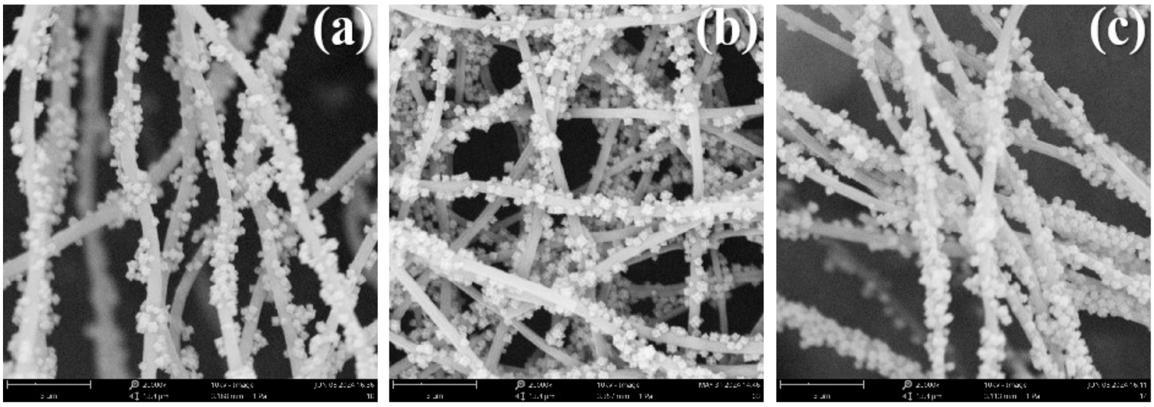

Fig. S2 (a), (b), (c) and (d) SEM images of the Co-Zn/CNFs-4, Co-Zn/CNFs-1 and Co/CNFs, respectively.

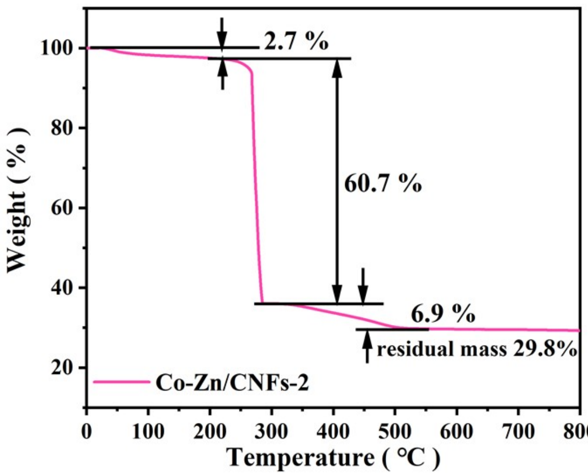

Fig. S3 TGA curve of Co-Zn/CNFs-2.

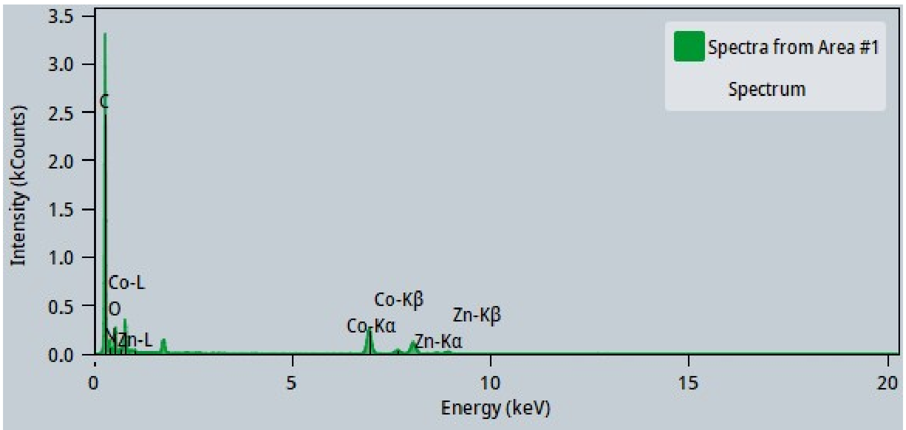

Fig. **S4** EDX spectrum of Co-Zn/CNFs-2

Table S1 ICP-MS of Co-Zn/CNFs-2

Element	Co/wt%	Zn/wt%	Co/Zn atomic ratio
Atomic fraction (%)	18.41	1.10	31.2/1.7

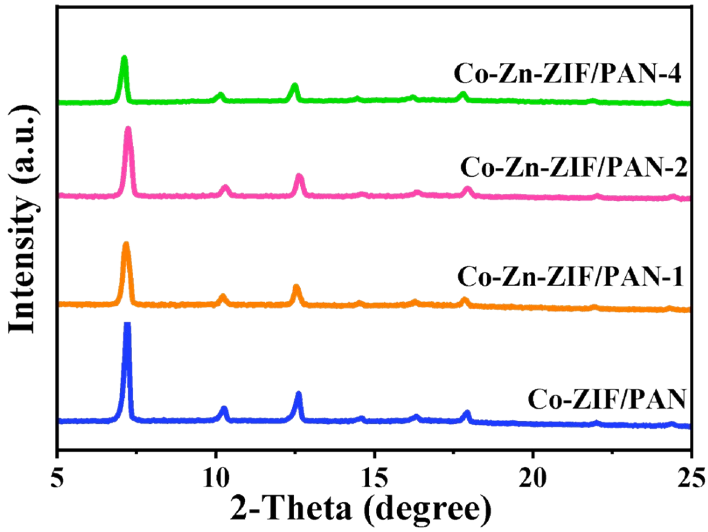

Fig. S5 XRD patterns of Co-Zn-ZIF/PAN-4, Co-Zn-ZIF/PAN-2, Co-Zn-ZIF/PAN-1 and Co-ZIF/PAN.

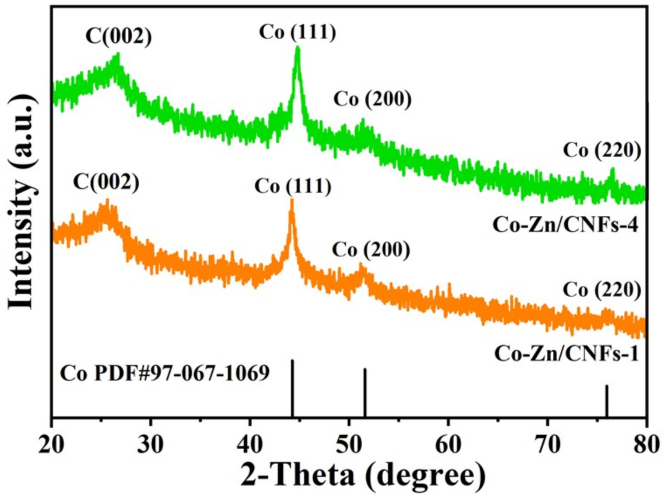

Fig. S6 XRD patterns of Co-Zn/CNFs-4 and Co-Zn/CNFs-1.

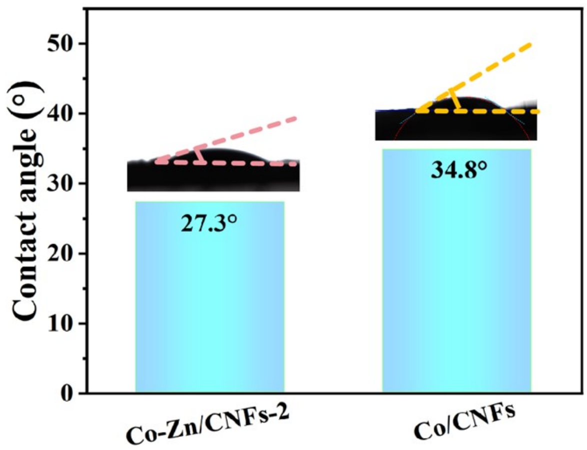

Fig. S7 Contact angles patterns of Co-Zn/CNFs-2 and Co/CNFs.

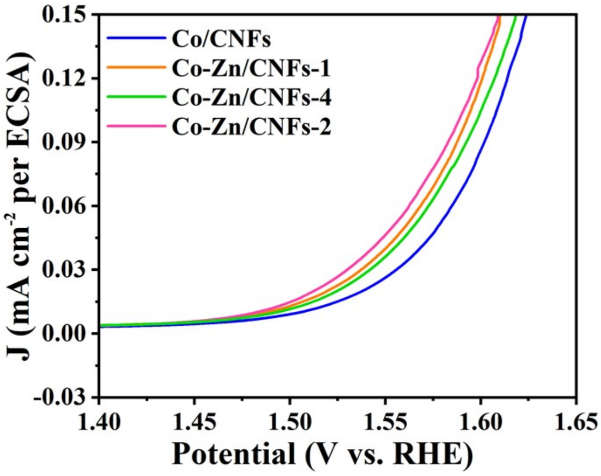

Fig.S8 ECSA-normalized LSV curves of different catalysts

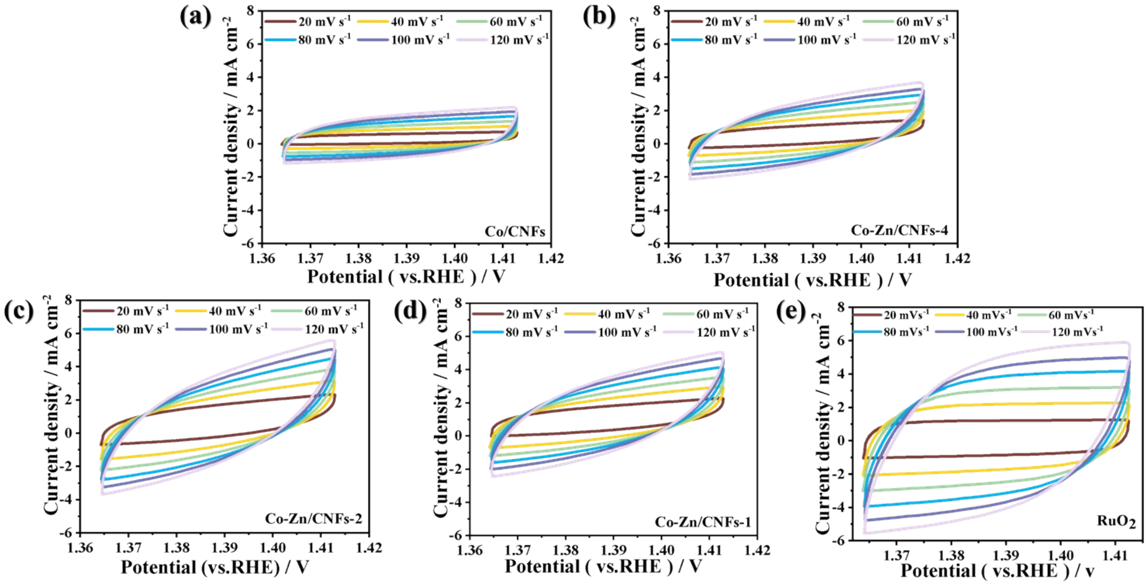

Fig. S9 The CV measurements in a non-faradic current region of (a) Co/CNFs, (b) Co-Zn/CNFs-4, (c) Co-Zn/CNFs-2, (d) Co-Zn/CNFs-1 and (e) RuO_2 at different scan rates of 20, 40, 60, 80, 100, and 120 mV s^{-1}.

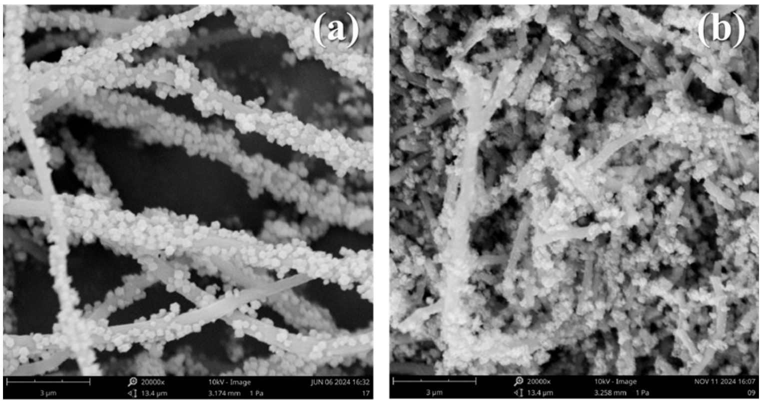

Fig. S10 (a) and (b) SEM images of the Co-Zn/CNFs-2 before and after OER test.

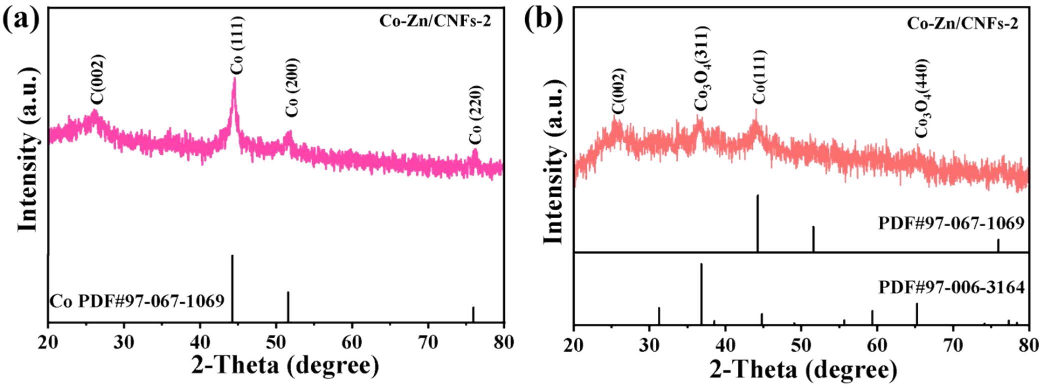

Fig. S11 (a) and (b) XRD patterns of Co-Zn/CNFs-2 before and after OER test.

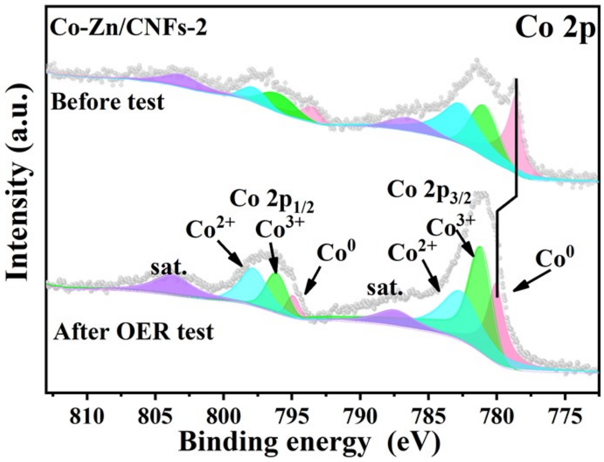

Fig. S12 XPS spectrum image of Co-Zn/CNFs-2 before and after OER test.

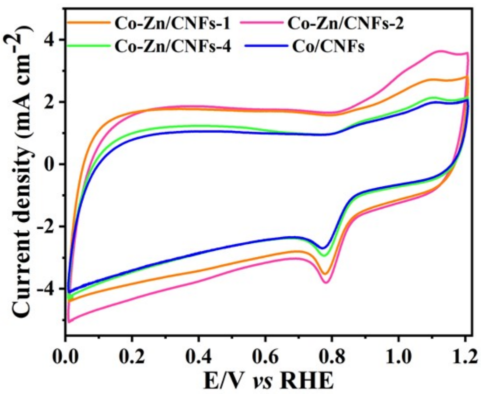

Fig. S13 CV curves of different catalysts in O_2-saturated 0.1M KOH

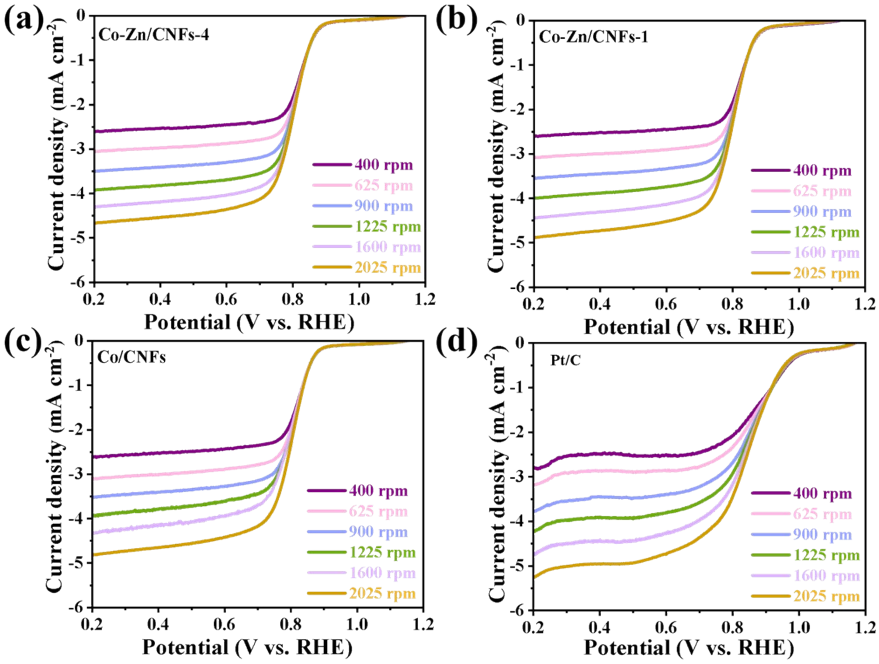

Fig. S14 (a), (b) and (c) LSV curves of Co-Zn/CNFs-4, Co-Zn/CNFs-1 and Co/CNFs samples at different rotation rates.

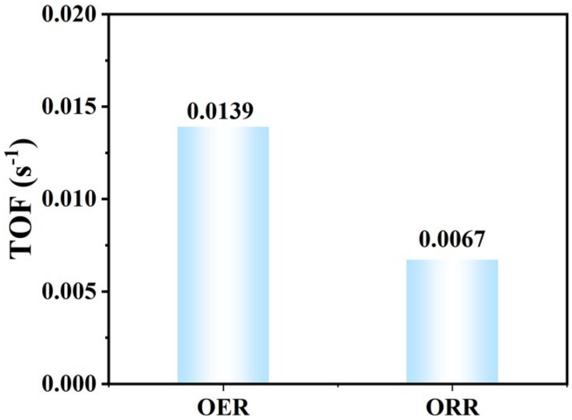

Fig. S15 The TOF values for Co-Zn/CNFs-2 toward OER and ORR process.

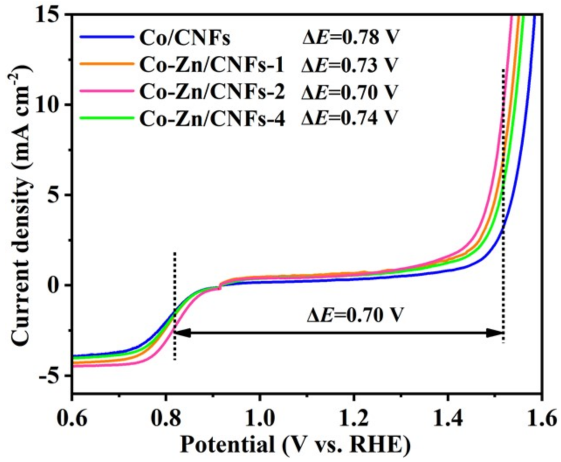

Fig. S16 Comparison of bifunctional activities of different samples

Table S2 Comparison of the OER and ORR performance of different catalysts

Catalyst	$E_{j=10}$ (V vs. RHE)	$E_{1/2}$ (V vs. RHE)	ΔE	Reference
Co-Zn/CNFs-2	1.52	0.816	0.70	This work
Co/Zn@NCF	1.69	0.84	0.85	Chemical Engineering Journal, 2023, 477: 147022
S-Co/CoNC	1.53	0.81	0.72	Materials Today Physics, 2023, 37: 101209
CNFs/CoZn-MOF@COF	1.57	0.82	0.75	Journal of Colloid and Interface Science, 2024, 666: 35
ZnCoFe-N-C	1.60	0.878	0.72	Small, 2023, 19(30): 2300612

CoNC-HCNFs	1.58	0.83	0.75	International Journal of Hydrogen Energy, 2023, 48(13): 5095
CoNi/Ti4O7@NS-CNFs	1.524	0.86	0.66	Journal of Colloid and Interface Science, 2023, 630: 763
ES-Co/Zn-CNZIFs	1.692	0.857	0.83	Journal of Energy Chemistry, 2023, 83:138
Co-N@PCNFs-0.2	1.66	0.87	0.79	ACS Sustainable Chemistry &Engineering, 2021, 9: 17068
NiFe-LDH/Co,N-CNF	1.542	0.790	0.75	Advanced Energy Materials, 2017, 7(21): 1700467
Co-N-CCNFMs	1.559	0.84	0.719	Energy Storage Materials, 2022, 47: 365
Co@Fe-CNFs-1000	—	0.81	—	Chinese Journal of Polymer Science, 2023, 41(12): 1889
ZIF-67@FeCo-NFs	1.62	0.89	0.73	Materials Today Energy, 2021, 20: 100682
CoZn/N-CNFs	—	0.814	—	Journal of Alloys and Compounds, 2023, 932: 167458
NiFe@C@Co CNFs	1.599	0.87	0.73	Small, 18(16): 2200578
Co/IMCCNFs	—	0.82	—	Nano-Micro Letters, 2019, 11: 1
Co–Fe–Zn@N-CNT/CNF	1.556	0.84	0.716	Inorganic chemistry, 2024, 63(9): 4373

Table S3 Comparison of the peak power density of Zn-air batteries with various electrocatalysts

Catalyst	**Peak power density ($mW\ cm^{-2}$)**	**Reference**
Co-Zn/CNFs-2	318.22	This work

ZnCo-NC-II	161.85	Applied Catalysis B: Environmental, 2022, 316: 121591.
CNFs/CoZn-MOF@COF	203.63	Journal of Colloid and Interface Science, 2024, 666: 35-46
ZnCoFe-N-C	137.8	Small, 2023, 19(30): 2300612
Co-N-C/CNF	159	Nano Research, 2023, 16(1): 545
CoZn/N-CNFs	223.8	Journal of Alloys and Compounds, 2023, 932: 167458
Co/Zn@NCF	202	Chemical Engineering Journal, 2023, 477: 147022
CoNi/Ti_4O_7@NS-CNFs	165.7	Journal of Colloid and Interface Science, 2023, 630: 763-771
Co-N@PCNFs-0.2	151	ACS Sustainable Chemistry &Engineering, 2021, 9, 17068-17077