Supplementary Information

FeCo/N-co-doped 3D Carbon Nanofibers as Efficient Bifunctional Oxygen Electrocatalyst for Zn-Air Batteries

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Chemical reagents and Materials

Potassium ferricyanide ($K_3[Fe(CN)_6]$), cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$), trisodium citrate dihydrate ($C_6H_5Na_3O_7$) obtained at Sinopharm Chemical Reagent Co., Ltd., China. 20 wt% Pt/C and RuO_2 acquired at Aladdin Co., Ltd., China. 5 wt% Nafion was obtained from Chuxi Co., Ltd., Shanghai, China.

Calculations

Koutecky–Levich equation was used to determine the number of electrons transferred (n) for ORR and to plot corresponding K-L curves at different potentials.

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \quad (1)$$

$$B = 0.2nFC_0 D_0^{2/3} v^{-1/6} \quad (2)$$

J is measured current, J_k is kinetic current density, ω is the rotation speed of RDE and B is the slope of K-L plots. In addition, n is the transferred electron number, F is Faraday constant (96 485 C/mol), C_0 is oxygen concentration in solution (1.2×10^{-6} mol/cm^3), D_0 is diffusion coefficient of O_2 in 1 M KOH ($1.9 \times 10{-}5$ cm^2/s) and v is the kinetic viscosity of the electrolyte (0.01 cm^2/s).

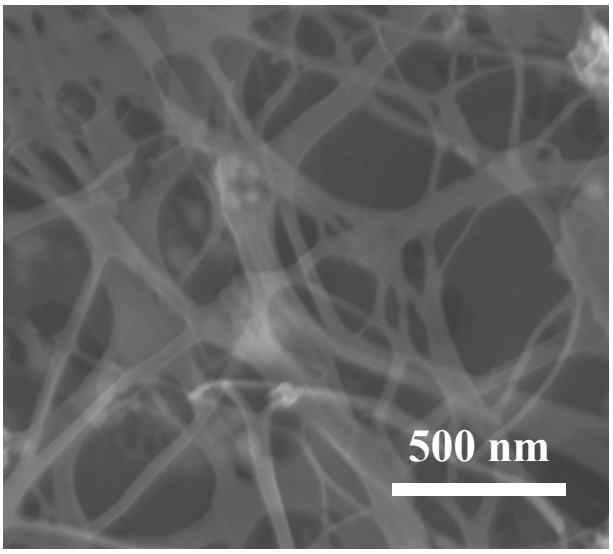

Fig. S1 SEM pattern of BC nanofibers after carbonization

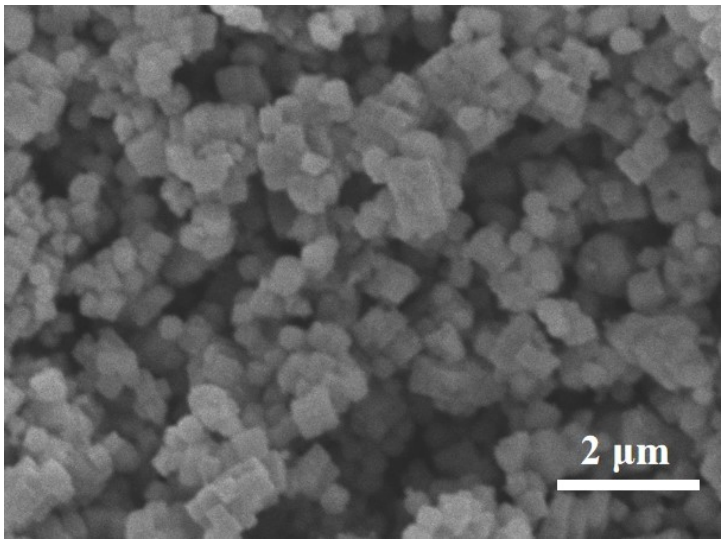

Fig. S2 SEM pattern of PBA nanoparticles before carbonization

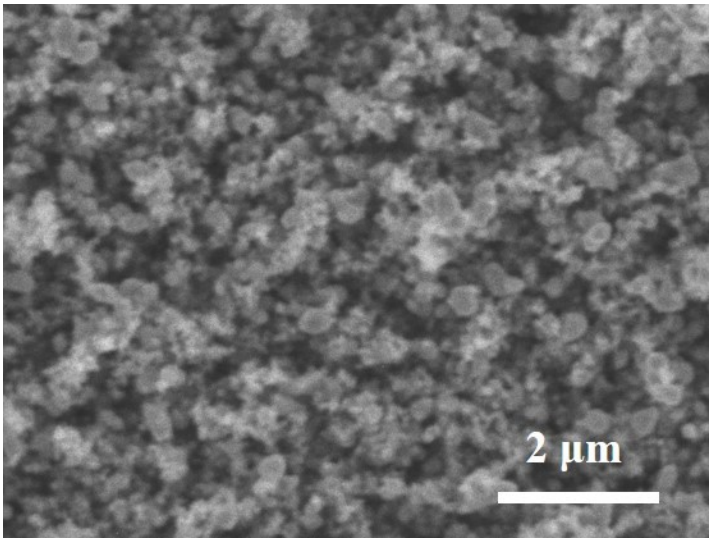

Fig. S3 SEM pattern of PBA nanoparticles after carbonization

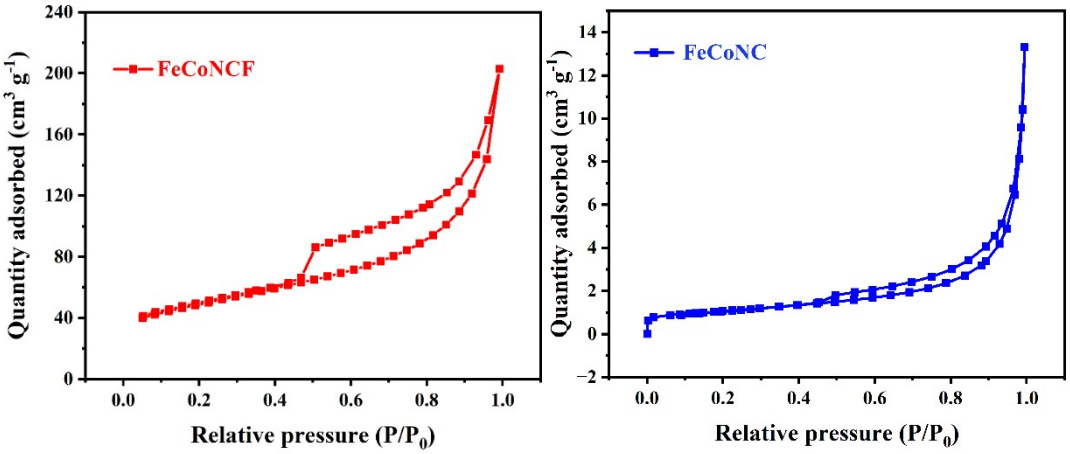

Fig. S4 N_2 adsorption−desorption isotherms of FeCoNCF and FeCoNC

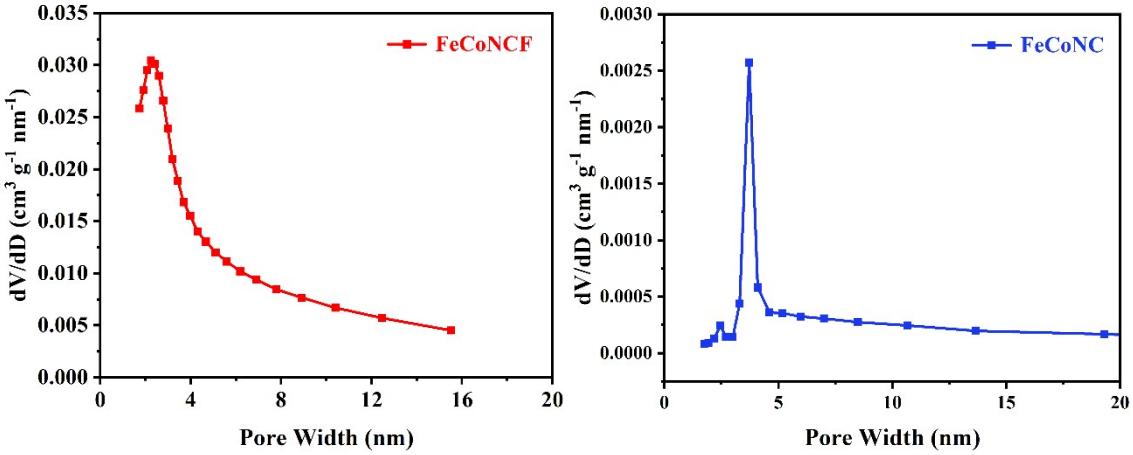

Fig. S5 Pore diameter distributions determined by BET method of FeCoNCF and FeCoNC

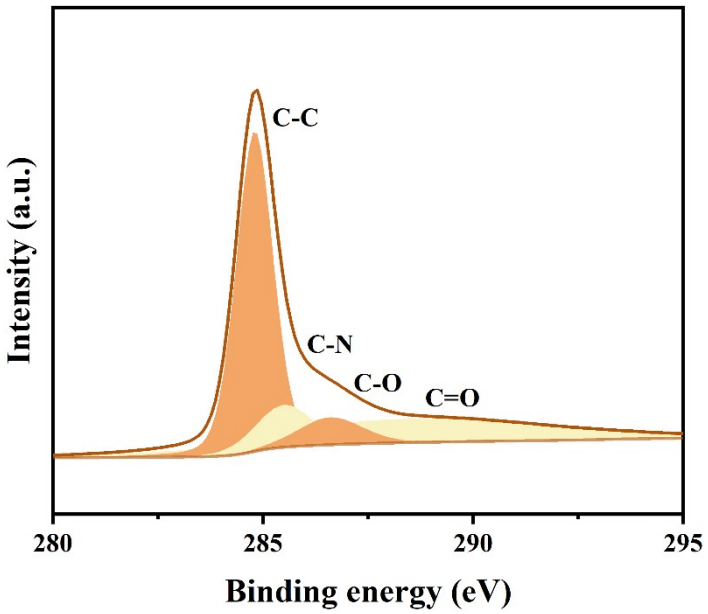

Fig. S6 High-resolution XPS survey spectrum of C 1s of FeCoNCF sample

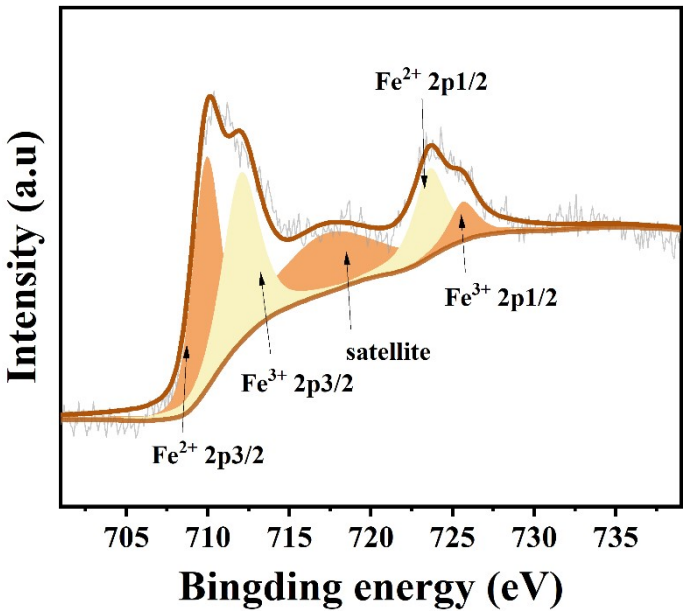

Fig. S7 High-resolution XPS survey spectra of Fe 2p of FeCoNC

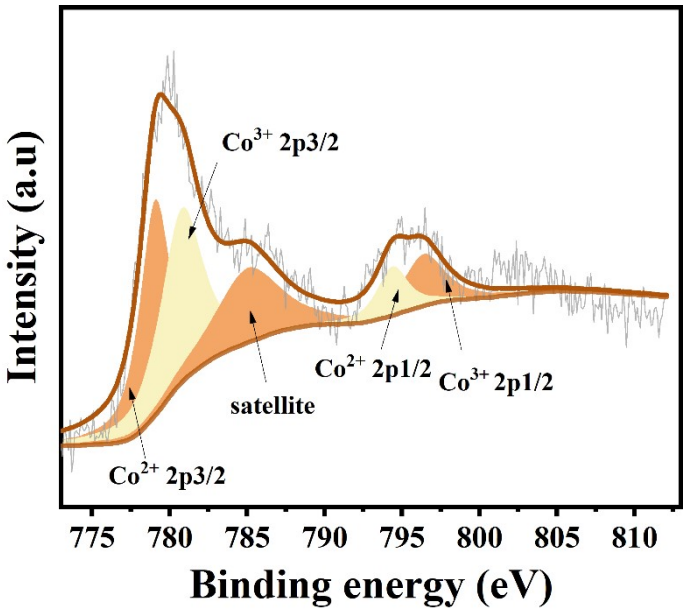

Fig. S8 High-resolution XPS survey spectra of Fe 2p of FeCoNCF and FeCoNC

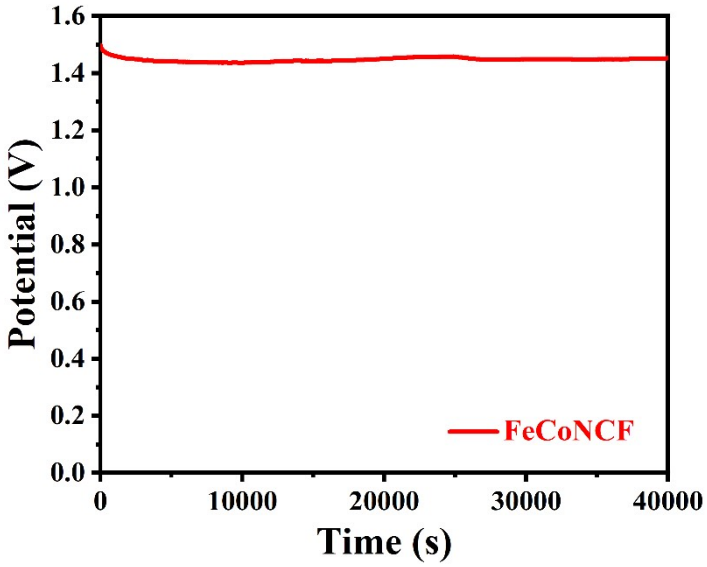

Fig. S9 Chronopotentiometry curve for FeCoNCF at 10 mA cm^{-2}

Table S1 Comparison of ORR and OER performance of FeCoNCF catalyst with transition metal-based electrocatalysts in reported in literatures.

Catalysts	**ORR activity** (**$E_{1/2}$**: Half-wave potential; **TS**: Tafel slope)	**OER activity** (**η_{10}**: Overpotential at current density of 10 mA cm^{-2})	**ΔE** (**ΔE**= $E_{j=10}$- $E_{1/2}$)	**Ref.**
FeCoNCF	$E_{1/2}$: 0.81 V TS: 51 mV dec^{-1}	η_{10}: 341 mV TS: 69 mV dec^{-1}	0.761	**This work**
NiFe/N-CNT	$E_{1/2}$: 0.75 V TS: /	η_{10}: 290 mV TS: 49 mV dec^{-1}	0.77	1

FeP/Fe_2O_3@NPCA	$E_{1/2}$: 0.81 V TS: 88 mV dec^{-1}	η_{10}: 402 V TS: 86 mV dec^{-1}	0.822	2
MnO/Co/PGC	$E_{1/2}$: 0.78 V TS: 69 mV dec^{-1}	η_{10}:307 mV TS: 77 mV dec^{-1}	0.757	3
Co@N-CNT/rGO-0.1	$E_{1/2}$: 0.82 V TS: 77 mV dec^{-1}	η_{10}: 480 mV TS: 251 mV dec^{-1}	0.89	4
FeCo-NSCNF@NCNT	$E_{1/2}$: 0.79 V TS: 64.5 mV dec^{-1}	η_{10}: 360 mV TS: 49.5 mV dec^{-1}	0.8	5
FeCo@NCNF	$E_{1/2}$: 0.825 V TS: 58 mV dec^{-1}	η_{10}: 344 mV TS: 56.6 mV dec^{-1}	0.749	6
FeCo-1/NSC	$E_{1/2}$: 0.82 V TS: 69.75 mV dec^{-1}	η_{10}: 325 mV TS: 56.6 mV dec^{-1}	0.735	7
FeCo/N-DNC	$E_{1/2}$: 0.81 V TS: /	η_{10}: 390 mV TS: 68 mV dec^{-1}	0.81	8
FeS_2–CoS_2/NCFs	$E_{1/2}$: 0.81 V TS: 55 mV dec^{-1}	η_{10}: 340 mV TS: 49 mV dec^{-1}	0.76	9
Co/CNWs/CNFs	$E_{1/2}$: 0.82 V TS: 107 mV dec^{-1}	η_{10}: 412 mV TS: 141 mV dec^{-1}	0.822	10
FeCo@NC-750	$E_{1/2}$: 0.80 V TS: 54.6 mV dec^{-1}	η_{10}: 290 mV TS: 52 mV dec^{-1}	0.72	11

Table S2 Comparison of Zn-air performance of FeCoNCF catalyst with transition metal-based electrocatalysts in reported in literatures.

Catalysts	**OCV (V)** (**OCV**: Open-circuit voltage; **L**=liquid ZAB; **S**=Solid ZAB)	**Power density (mW cm^{-2})** (**A**= Aqueous ZAB; **S**=Solid-state ZAB)	**Ref.**
FeCoNCF	1.46 V (S)	FeCoNCF: 49.29 mW cm^{-2} (S) Pt/C+RuO_2: 30.91 mW cm^{-2} (S)	**This work**
NiFe/N-CNT	1.48 V (A) 1.41 V (S)	NiFe/N-CNT: 300.7 mW cm^{-2} (A) Pt/C+RuO_2: 105.6 mW cm^{-2} (A) NiFe/N-CNT: 105.4 mW cm^{-2} (S)	1
FeP/Fe_2O_3@NPCA	1.42 V (S)	FeP/Fe_2O_3@NPCA: 130 mW cm^{-2} (A) Pt/C+RuO_2: 108 mW cm^{-2} (A) FeP/Fe_2O_3@NPCA: 40.8 mW cm^{-2} (S)	2
MnO/Co/PGC	1.52 V (A)	MnO/Co/PGC: 172 mW cm^{-2} (A) Pt/C+RuO_2: 150 mW cm^{-2} (A)	3
Co@N-CNT/rGO-0.1	1.43 V (A)	Co@N-CNT/rGO-0.1: 122 mW cm^{-2} (A) Pt/C+RuO_2: 102 mW cm^{-2} (A)	4
FeCo-NSCNF@NCNT	/	/	5
FeCo@NCNF	1.46 V (A)	FeCo@NCNF: 134.83 mW cm^{-2} (A) Pt/C+RuO_2: 91.24 mW cm^{-2} (A)	6
FeCo-1/NSC	1.45 V (A)	FeCo-1/NSC: 162.74 mW cm^{-2} (A) Pt/C+RuO_2: 96.05 mW cm^{-2} (A) FeCo-1/NSC: 68.3 mW cm^{-2} (S) Pt/C+RuO_2: 28.2 mW cm^{-2} (S)	7

FeCo/N-DNC	/	FeCo/N-DNC: 115 mW cm^{-2} (A) Pt/C+RuO_2: 109 mW cm^{-2} (A)	8
FeS_2–CoS_2/NCFs	1.46 V (L) 1.39 V (S)	FeS_2–CoS_2/NCFs: 257 mW cm^{-2} (L) Pt/C+RuO_2: 163 mW cm^{-2} (L) FeS_2–CoS_2/NCFs: 69 mW cm^{-2} (S)	9
Co/CNWs/CNFs	1.46 V (L) 1.55 V (S)	Co/CNWs/CNFs: 304 mW cm^{-2} (L) Pt/C+RuO_2: 106 mW cm^{-2} (L) Co/CNWs/CNFs: 176 mW cm^{-2} (S)	10
FeCo@NC-750	1.38 V (L)	FeCo@NC-750: 132 mW cm^{-2} (L) Pt/C+RuO_2: 136 mW cm^{-2} (L)	11

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