Supplementary Information (SI) for Chemical Communications.

Supporting Information

Weaving Hollow Fiber Structure with Transition Metal Catalyst for Zinc-Air Batteries

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Experimental section

Materials:

Tetrapropoxysilane and 1tetraethyl orthosilicate were purchased from Meryer Chemical Technology Co., Ltd., ammonia (25-28%) water and dimethylformamide (DMF) were purchased from Sinopharm Group, formaldehyde (37-40%) and resorcinol were Shanghai Adamas Reagent Co., Ltd., hydrofluoric acid solution (40wt%), Nafion, $Zn(Ac)_2$ and KOH were from Shanghai Aladdin Biochemical Technology Co.,Ltd., Polyacrylonitrile and Cobalt (II) 4-oxopent-2-en-2-olate were purchased from Sigma-Aldrich. Iron (III) acetylacetonate was brought from Alfa Aesar, Super P was brought from DoDochem.

The preparation of Hollow Carbon Spheres (HCS): 7 mL of tetrapropoxysilane and 7 mL of tetraethyl orthosilicate were added with to a mixture composed of 280 mL of ethanol and 40 mL of ultrapure water. Then, 12 mL of ammonia water was added dropwise to the mixed solution. Subsequently, 1.6 g of resorcinol and 2.25 mL of formaldehyde were added sequentially and stirred at room temperature for 24 hours to obtain resorcinol-formaldehyde resin (RF). Carbonization of the composites was done at 800 ℃ for 3 h under N_2 after centrifugation, followed by etching using 40 wt% hydrofluoric acid solution to give pristine HCSs.

The preparation of Electrospun Fibers (CF): 1 g of PAN was first added to 7.4 mL of DMF solution and magnetically stirred at 500 rpm for 12 hours at 60 ℃ to ensure complete dissolution. The solution was electrospun using a computer-controlled high power voltage supply, with a voltage of around 12 kV. Then, the spun fibers underwent multiple pyrolysis treatments. Initially, the sample undergoes a pre-oxidation process by heating in air at 280 °C for 2 h, followed by carbonization at 800 °C for 3 h under N_2. The obtained carbon fiber support was labeled CF.

The preparation of Hollow Carbon Sphere Electrospun Fiber (N@HCF) Composites: 1 g of PAN and 0.2 g HCS was added to 7.4 mL of DMF solution and magnetically stirred at 500 rpm for 12 hours at 60 °C to ensure complete dissolution. The solution was electrospun using a computer-controlled high power voltage supply, with a voltage of around 12 kV. Then, the spun fibers underwent multiple pyrolysis treatments. Initially, the sample undergoes a pre-oxidation process by heating in air at 280 °C for 2 h, followed by carbonization at 800 °C for 3 h under N_2. The obtained carbon fiber support was labeled N@HCF. The preparation of Iron-Based Hollow Carbon Sphere Electrospun Fiber (FeN@HCF) Composites: On the basis of N@HCF preparation, 1 mmol of iron(III) acetylacetonate was added to the spinning solution. The preparation of Cobalt-Based Hollow Carbon Sphere Electrospun Fiber (CoN@HCF) Composites: On the basis of N@HCF preparation, 1 mmol of cobalt(II) acetylacetonate was added to the spinning solution. The preparation of Iron-Cobalt-Based Hollow Carbon Sphere Electrospun Fiber (FeCoN@HCF) Composites: On the basis of N@HCF preparation, 0.5 mmol of iron(III) acetylacetonate and 0.5 mmol of cobalt(II) acetylacetonate was added to the spinning solution.

Material Characterizations:

SEM and TEM were used to analyze the internal structure of the catalyst samples, with EDS attached to the TEM for elemental distribution analysis. Raman spectroscopy

(500-3500 cm^{-1}) using an HR800 laser confocal spectrometer revealed the carbon structure. XRD, with a CuKα source (10-80° at 20° min^{-1}), characterized the crystal structure. X-ray photoelectron spectroscopy (XPS) was employed to characterize the surface composition and chemical valence states of C, N, O, Fe, and Co in the materials.

Oxygen Electrocatalysis Performance Testing

Electrochemical tests were conducted on a standard three-electrode system. Hg/HgO and Pt foil served as reference and counter electrodes. The catalyst ink for the working electrode involved mixing 5 mg of the catalyst with 280 μL of water, 700 μL of ethanol, and 20 μL of Nafion solution. Subsequently, the ink was drop-cast onto the surface of the glassy carbon electrode and allowed to dry in the air.

The ORR polarization curves were collected from 0.2 V to -0.8 V using a rotating disk electrode test at a scan rate of 10 mV s^{-1} with a rotating speed of 1600 rpm in an O_2-saturated 0.1 M KOH solution. And the OER polarization curves were recorded from 0.1 V to 1 V at a scan rate of 10 mV s^{-1}.

The reference potentials were converted to the reversible hydrogen electrode (RHE) potential using the Nernst equation for consistency. Then we perform *iR* compensation.

$$E(RHE) = E(Hg/HgO) + 0.0591 * pH + 0.097$$

Assembly and Testing of Zinc-Air Battery

The rechargeable zinc-air battery was self-assembled using a pretreated zinc sheet as the anode, a composite air cathode loaded with the catalyst, and a mixed electrolyte containing 0.2 M $Zn(Ac)_2$ and 6 M KOH. The air cathode was prepared by mixing 25 mg of catalyst, 6.25 mg of Super P, 900 μL ethanol, and 100 μL Nafion solution, stirring for 12 hours, and coating onto hydrophobic carbon paper, followed by vacuum drying at 60 °C for 12 hours. The electrochemical performance of the assembled zinc-air battery was tested using the NEWARE battery test system and the CHI630E electrochemical workstation.

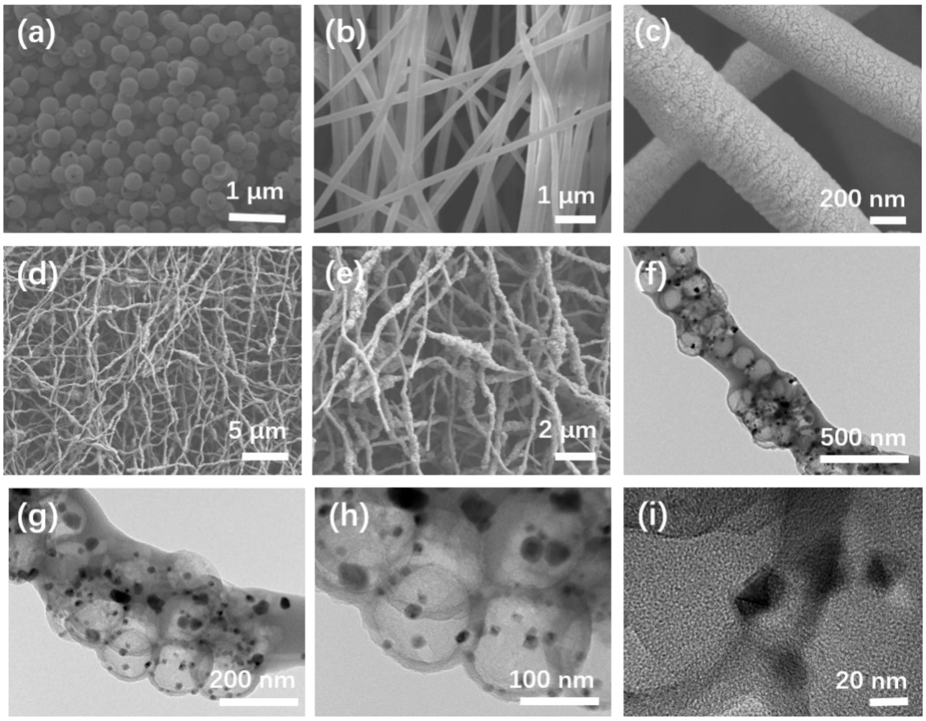

Fig. S1 SEM images of (a) HCS, (b-c) CF and (d-e) FeCoN@HCF; (f-i) TEM images of FeCoN@HCF.

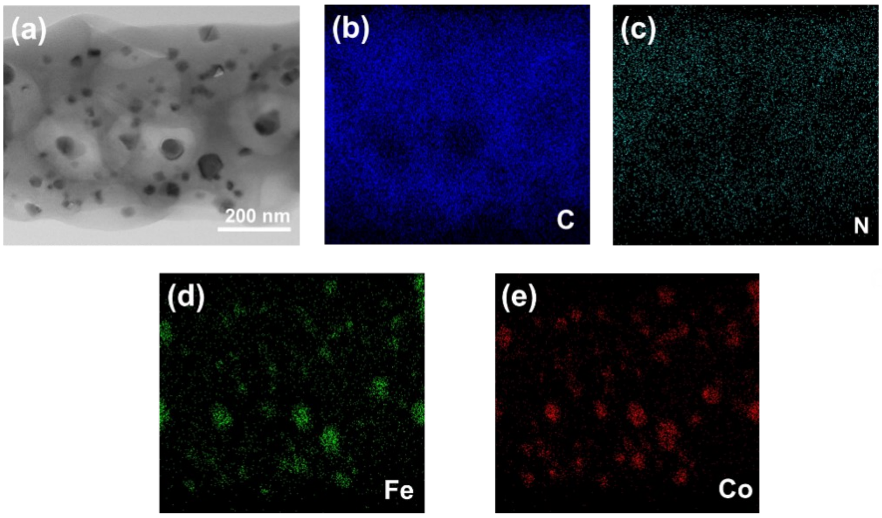

Fig. S2 EDS image of FeCoN@HCF and the corresponding element mappings.

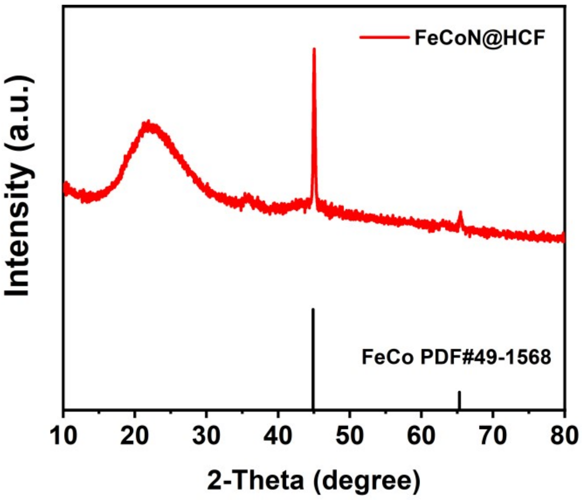

Fig. S3 XRD pattern of FeCoN@HCF.

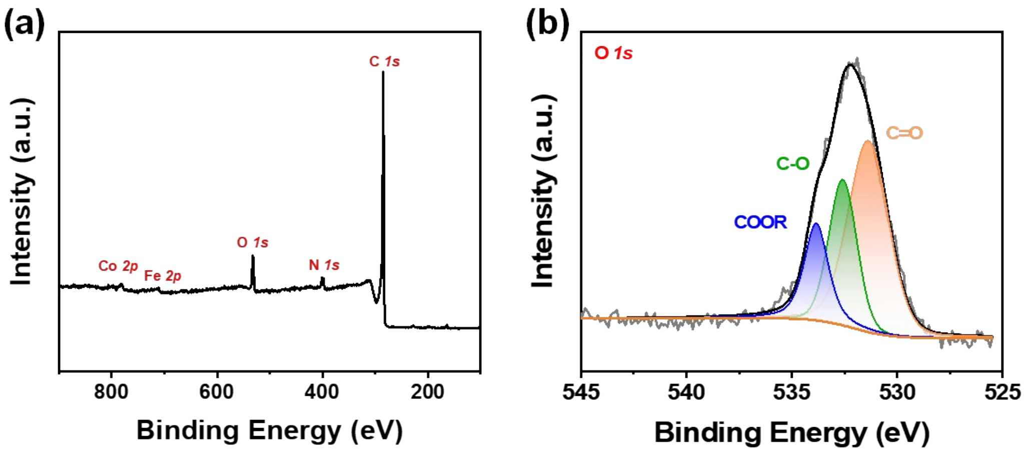

Fig. S4 (a) XPS survey spectrum of FeCoN@HCF; (b) High-resolution XPS spectrum of O *1s*.

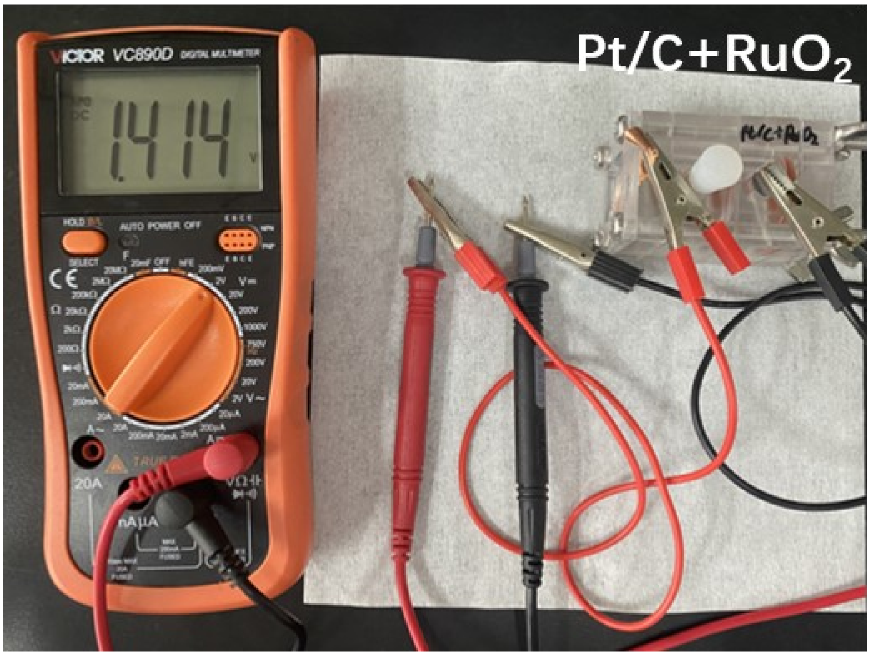

Fig. S5 Open-circuit voltage curves of alkaline zinc-air batteries assembled based on Pt/C + RuO_2.

Tab. S1. Comparison of main parameters for this work with related references

Catalyst	**ORR ($E_{1/2}$)**	**Tafel slope (mV dec^{-1})**	**OER ($E_{j=10\ mA\ cm-2}$)**	**Tafel slope (mV dec^{-1})**	**Specific capacity (mAh g^{-1})**	**Cycling stability**	**Cycling Current density (mA cm^{-2})**	**Reference**
FeCoN@HCF	**0.80 V**	**99**	**1.65 V**	**59**	**782**	**1000 h**	**5**	**This work**
$Ni_{0.6}Fe_{2.4}O_4$@NC-1	0.86 V	84.3	1.54 V	56	800	300 h	10	1
300NiFe-Mi-C	0.83 V	98	1.56 V	57	805	100 h	10	2
3D CuCo-NC	0.89 V	61	1.63 V	102	810	600 h	10	3
Co–N–mC	0.76 V	60	1.67 V	118	718	100 h	5	4
MC@NC-0.3	0.82 V	85	1.59 V	77	776	300 h	10	5

Reference：

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