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Supporting Information

Coordination polymer derived Fe-N-C electrocatalyst with high performance for oxygen reduction reaction in Zn-air batteries

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1. Materials and Characterizations.

All reagents and solvents utilized in this paper were of analytical grade, which were obtained from commercial suppliers and were used directly without further purification. Aqueous solutions were prepared from high purity water (⩾18.25 MΩ·cm). Carbon black (Black Pearls 2000) was obtained from Cabot Corporation. 5,10,15,20-tetraphenyl-21H,23H-porphyrin iron (III) chloride, Fe(TPP)Cl, was obtained from Energy Chemical Corporation. Pt/C (20% Pt/Vulcan XC-72, Johnson Mattey, HiSPEC 3000). Powder X-ray diffraction (PXRD) measurements were performed on an X-ray powder diffractometer (D/max2550 V, Rigaku Japan) in the range 5-80° at room temperature. Materials' morphologies were recorded on Transmission electron microscopy (TEM) and HR-TEM (ThermoFisher Talos F200X) operating at 100 kV. N_2 adsorption-desorption data were examined at liquid nitrogen temperature (77 K) on a Micromeritics ASAP 2010 M apparatus. Raman spectra were performed on Renishaw 2000 instrument with a 532 nm excitation wavelength to obtain graphitization degree (I_D/I_G) of the samples. The Brunauer-Emmett-Teller (BET) method was used to calculate the catalyst surface areas. X-ray photoelectron spectroscopy (XPS) spectra were conducted on a Thermo Escalab 250 instrument with a monochromatic Al Kα X-ray source

($h\nu$ =1486.6 eV), with binding energies referenced to the C1s peak (284.6 eV) corresponding to adventitious carbon. The metal contents of the samples were examined by ICP-AES (Perkin Elmer Ltd., USA).

2. The preparation of the coordination polymer (CP)

CP was prepared in a similar way as our previous report.[S1] $Zn(NO_3)_2{\cdot}6H_2O$ (1.487 g), 4,4'-oxybisbenzoic acid (1.291 g), and 4,4'-bipyridine (0.781 g) were added to a mixed solvent of deionized water (H_2O) and N,N-dimethylformamide (DMF) with the volume ratio 2:3. The mixture was stirred and sealed in a 50 mL Teflon-lined stainless-steel autoclave and heated at 120 °C for 24 h. After cooling to room temperature, the mixture was filtered, washed with DMF and H_2O, and dried to obtain the solid products of CP.

3. Electrochemical Measurement

The catalyst obtained (5.0 mg) was added to a 250 μL of mixture solution in a centrifuge tube with 5 wt% Nafion dispersion (Aldrich) and isopropanol in a volume ratio of 1:9. Then, the above mixture was sonicated for 1 h to obtain an even suspension (catalyst ink). 10 μL of catalyst ink was dropped onto the surface of glassy carbon disk (area: 0.196 cm^2), and dried naturally to obtain an even film with a catalyst mass loading of 1.0 mg cm^{-2}. The loading amount for the reference Pt/C catalyst was 0.3 mg cm^{-2}.

The electrochemical performance of the catalysts was evaluated on a CHI 760D electrochemical workstation using a rotating ring disc electrode (RRDE, Pine Instrument) in a standard three-electrode system. A graphite rod (diameter: 4.0 mm) was employed as the counter electrode. A Hg/HgO electrode was employed as the reference electrode. Cyclic voltammetry (CV) and linear scanning voltammetry (LSV) were recorded in O_2-saturated 0.1M KOH solution with a scan rate of 10 mV/s at room temperature. For catalyst durability test, the chronoamperometric response of the catalysts was evaluated at 0.55 V (vs. RHE) in O_2-saturated 0.1 M KOH solution at 900 rpm.

For RRDE measurement: The H_2O_2 yield and electron transfer number (n) were calculated from the RRDE data using the following equation (**1**) and equation (**2**)

$$H_2O_2\,\% = \frac{200\times I_r}{I_r + N\times I_d} \qquad \textbf{(1)}$$

$$n = \frac{4\times N\times I_d}{I_r + N\times I_d} \qquad \textbf{(2)}$$

where I_d is the disk current, I_r is the ring current, and N is the collection efficiency.

RHE (Reversible Hydrogen Electrode) calibration: The calibration of the reference electrode was conducted in a H_2-saturated electrolyte with Pt wire as the working electrode. The potential at which the current crossed zero was regarded as the thermodynamic potential for the hydrogen electrode reactions.

4. Zinc-air batteries (ZABs)

Zn-air batteries were constructed using polished Zn foil as the anode, catalyst loaded (1.0 mg cm^{-2}) carbon paper as the cathode, and aqueous solution of $ZnAc_2$ (0.2 M) and KOH (6.0 M) as the electrolyte. The reference sample of commercial 20 wt.% Pt/C-loaded ZABs were prepared with the same loading amount of 1.0 mg cm^{-2}. Measurement was performed on a CHI 760D electrochemical workstation at room temperature.

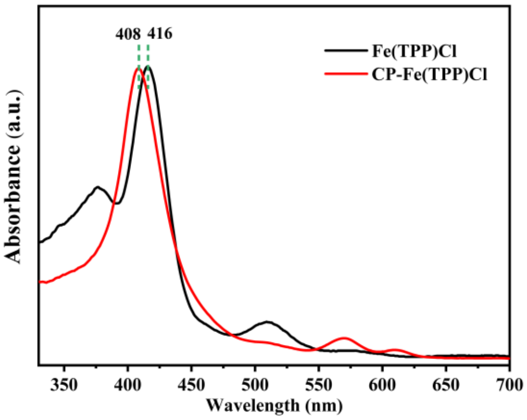

Figure S1. UV-vis diffuse reflectance spectra of Fe(TPP)Cl and Fe(TPP)Cl-loaded on CP.

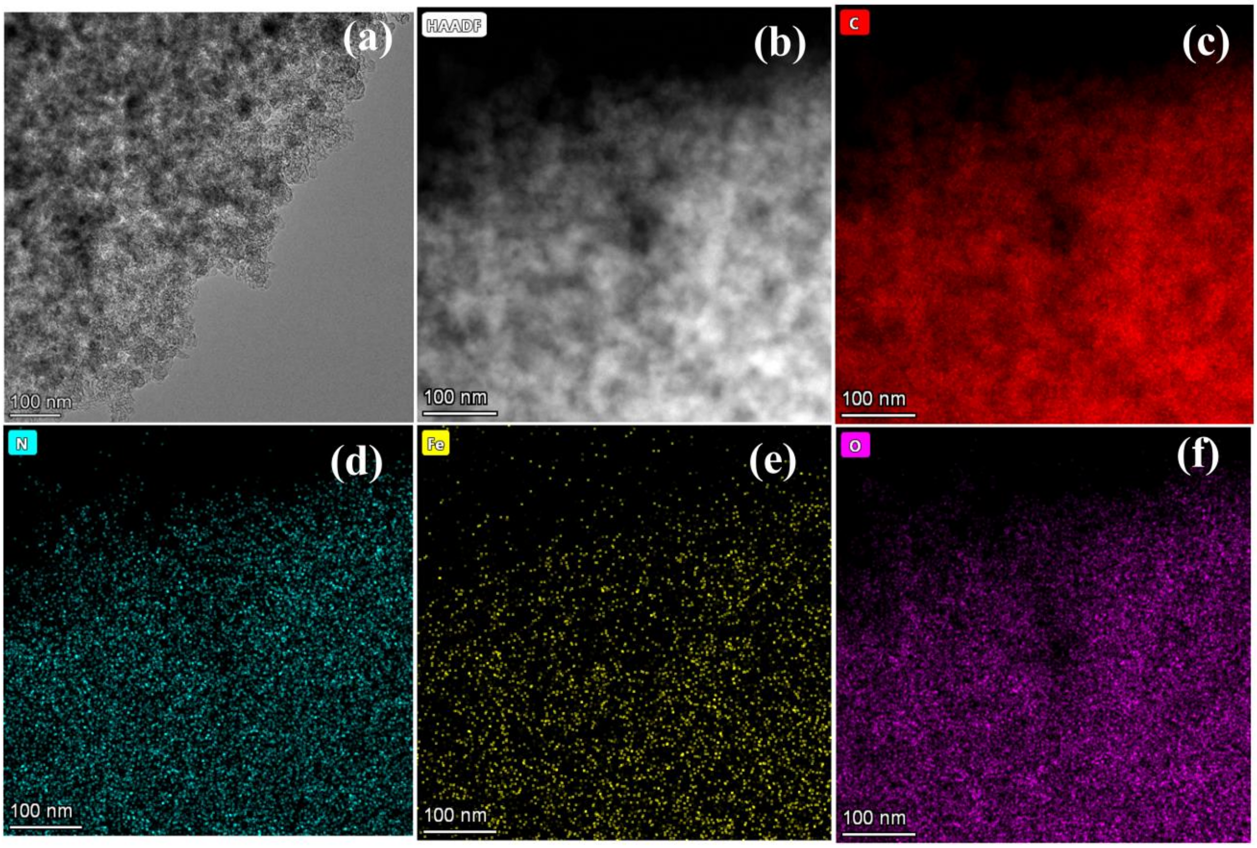

Figure S2. (a) The HR-TEM, **(b)** HADDF-STEM images, and **(c, d, e, f)** element mapping patterns of Fe/C.

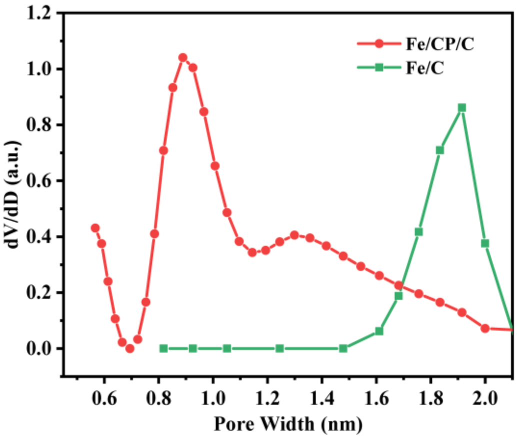

Figure S3. The pore size distribution of Fe/CP/C and Fe/C at 0-2 nm.

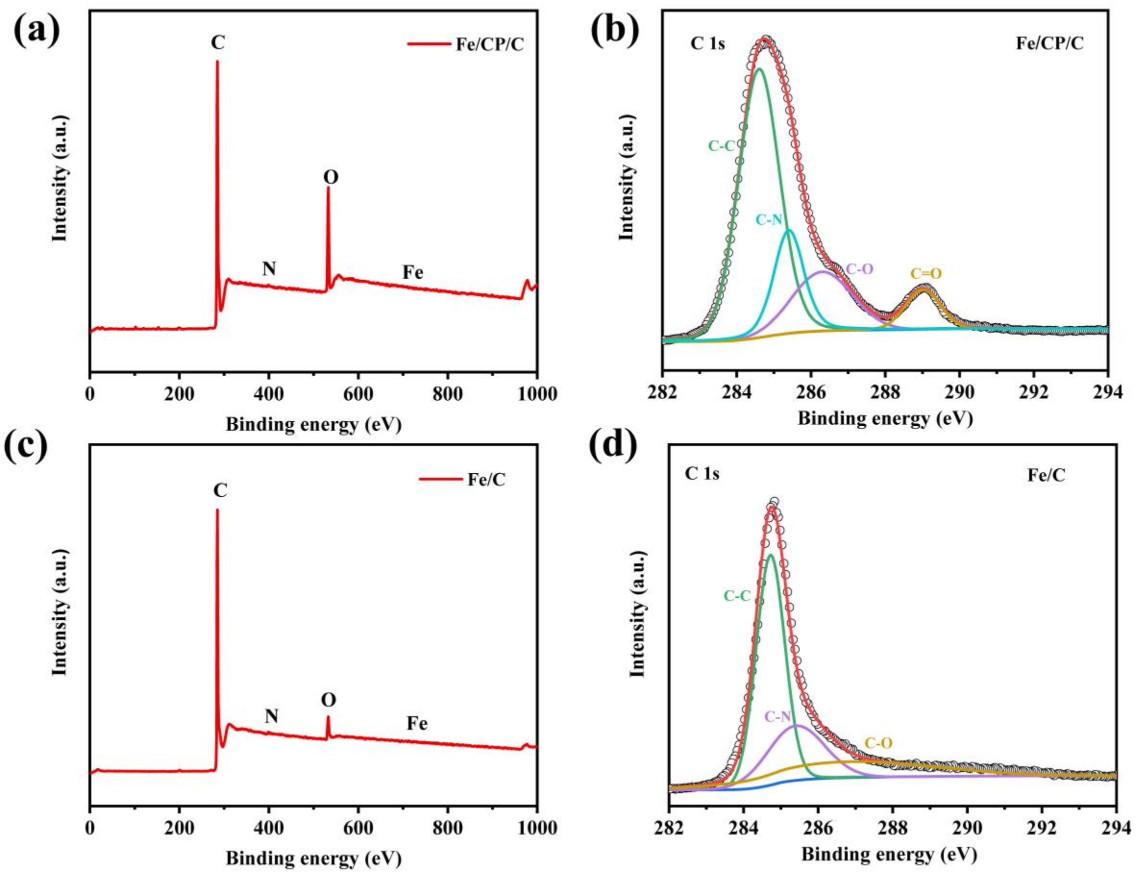

Figure S4. (a) XPS survey and **(b)** High-resolution C 1s XPS spectra of Fe/CP/C. **(c)** XPS survey and **(d)** High-resolution C 1s XPS spectra of Fe/C.

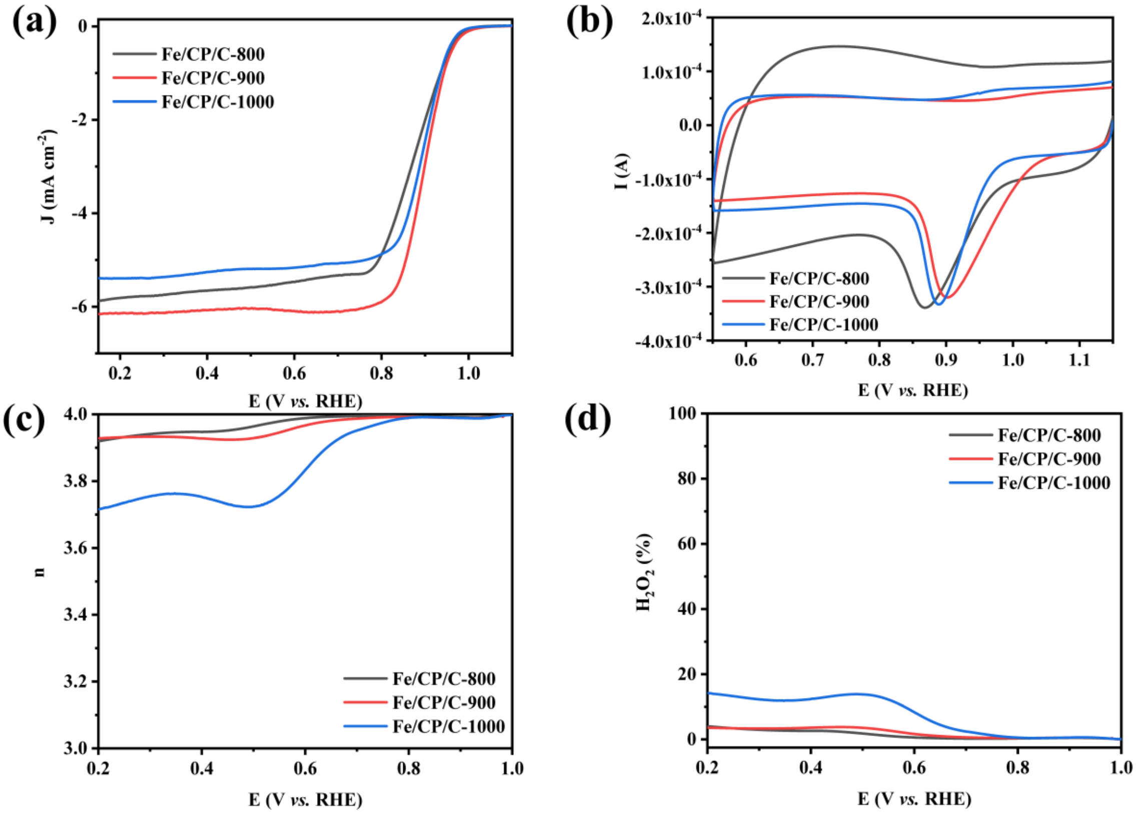

Figure S5. (a) LSV curves, **(b)** CV curves, **(c)** number of electrons transferred (n), and **(d)** H_2O_2 yields of the catalysts of Fe/CP/C-800, Fe/CP/C-900, and Fe/CP/C-1000 in O_2-saturated 0.1 M KOH at 1600 rpm.

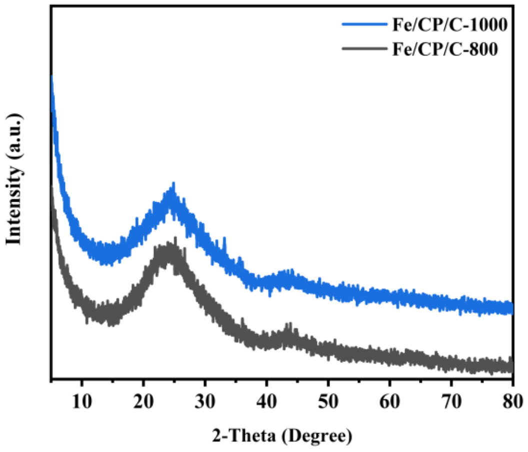

Figure S6. XRD patterns of Fe/CP/C-1000 and Fe/CP/C-800.

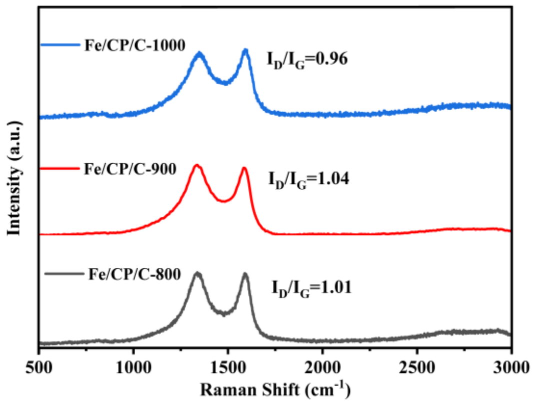

Figure S7. Raman pattern of Fe/CP/C-T (T = 800, 900, 1000)

Table S1. The different species of N contents in the catalysts determined by XPS.

Catalyst	Pyridinic-N	Fe-N	Graphitic- N	Oxidized-N
Fe/CP/C (%)	28.7	31.5	31.9	3.7
Fe/C (%)	17.8	29.9	41.9	10.4

Table S2. Performance of reported M-N-C catalysts in alkaline electrolyte.

#	Catalyst	$E_{1/2}$ (V vs. RHE)	Ref.
1	Fe/OES	0.85	S2
2	Fe-N/P-C-700	0.867	S3
3	Fe1-HNC-500-850	0.842	S4
4	FeCo@NC-g	0.89	S5
5	1.71% Fe-N/C-SAC	0.87	S6
6	Fe-1	0.882	S7
7	CoNC SAC	0.86	S8
8	Fe,Co,N−C	0.90	S9
9	Fe/CP/C	0.90	This work

Table S3. The R_{Ω} and R_{ct} for Fe/CP/C, Fe/C and Pt/C.

Catalyst	R_{Ω} (Ω)	R_{ct} (Ω)
Fe/CP/C	87	135
Fe/C	92	274
Pt/C	90	222

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