

Supporting Information

Small-size and well-dispersed Fe nanoparticles embedded in carbon rods for efficient oxygen reduction reaction

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S1. Experimental Section

All reagents were analytical grade and used without further purification. All solutions used in electrochemical experiments were prepared with Millipore water ($\geq 18 \text{ M}\Omega$).

Synthesis of Zn-MOF

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (14.9 mg, 0.05 mmol), 1,2,4-Benzenetricarboxylic acid (10.5 mg, 0.05 mmol) and MIDPPA (4,4'-di(4-pyridine)-4"-imidazoletriphenylamine) (23.3 mg, 0.05 mmol) was dissolved in 12 mL of DMF/ H_2O (1:2, V/V). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (20 mL) under autogenous pressure and heated at 130 °C for 3 d. Large quantity of yellow crystals were obtained, which were washed with mother liquid, and dried under ambient conditions.

Synthesis of Fe@Zn-MOF

Zn-MOF (10 mg) was placed in a 5-mL glass vial. This vial was placed in a glass bottle containing Fc (1.0, 2.5 and 4.0 mg named as Fe(10)@Zn-MOF, Fe(25)@Zn-MOF and Fe(40)@Zn-MOF). The bottle was sealed and then heated under 150 °C for 24 hours.

Synthesis of FeZn@NC-m

Fe@Zn-MOF added melamine (mass ratio: 1/10) was carbonized under N_2 atmosphere in a tube furnace, where the temperature was raised up from 30 °C to 800 °C at a heating rate of 5 °C/min. After holding at 800 °C for 2 hours, the temperature was cooled down to room temperature naturally to afford black powder. When the amount of Fc was tailored to 10, 25, and 40% of the mass of Zn-MOF, the corresponding products were marked as Fe(10)Zn@NC-m, Fe(25)Zn@NC-m, and Fe(40)Zn@NC-m, respectively. Zn@NC was synthesized by calcining Zn-MOF. Zn@NC-m was synthesized by calcining Zn-MOF and melamine.

Characterizations

Powder X-Ray diffraction (PXRD) patterns were recorded on a D8 DAVANCI X-ray powder diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The diffractometer was operated with working voltage and current of 40 kV and 40 mA, respectively. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on a JEM-2100 apparatus working at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) was carried out with a S-4800 (JEOL) apparatus working at an acceleration voltage of 2 kV. X-ray photon spectroscopy (XPS) was performed on an ESCA Lab250 X-ray microprobe corrected by C1s peak at 284.6 eV. Nitrogen sorption experiments and pore size distribution (PSD) were measured using an ASAP 2020 surface area detecting instrument by N₂ physisorption at 77 K. Prior to the measurement, the samples were degassed at 120°C for 6 h.

Electrochemical Measurements

All electrochemical experiments were conducted on a CHI 760 E electrochemical station (Shanghai Chenhua Co., China) in a standard three electrode cell in O₂-saturated 0.1 M KOH at room temperature. A glassy carbon electrode (GCE, 5 mm in diameter), a Hg/HgO electrode (SCE), and a Pt wire were used as the working, reference and counter electrode, respectively. All electrode potentials were expressed in reference to the reversible hydrogen electrode (RHE). 5 mg of the catalysts were dispersed in 1 mL of 1:1 v/v water/alcohol with 40 μ L Nafion by sonication to form a homogeneous suspension. Typically, 5 μ L well-dispersed suspension was dropped on the glassy carbon electrode and then dried in an ambient environment for measurements. Linear sweep voltammetry (LSV) was tested with a scan rate of 10 mV s⁻¹ at 1600 rpm on rotating disc electrode (RDE). The chronoamperometry (CA) was tested at an overpotential of 0.85 V vs RHE after equilibrium.

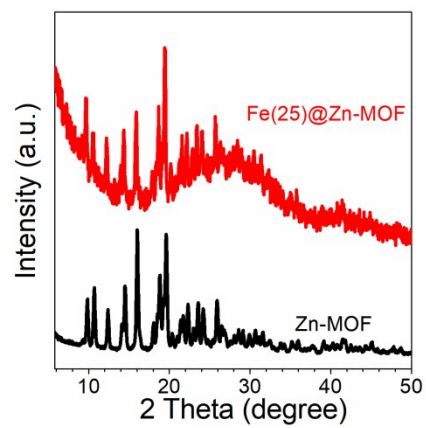


Fig. S1. XRD patterns of Zn-MOF and Fe(25)@Zn-MOF.

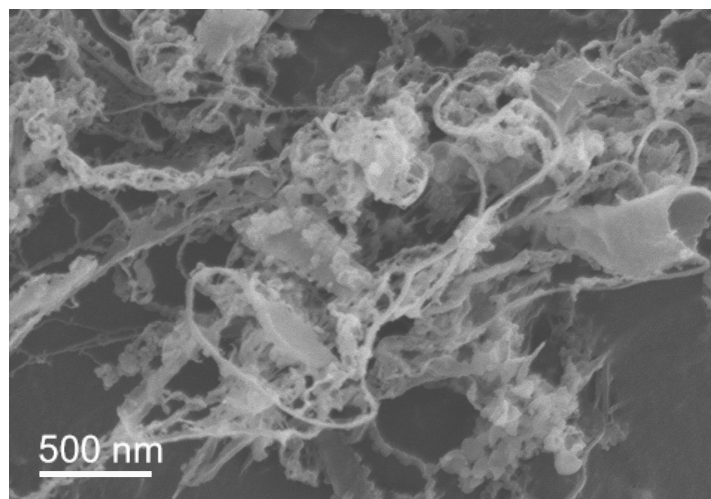


Fig. S2. SEM image of Fc.

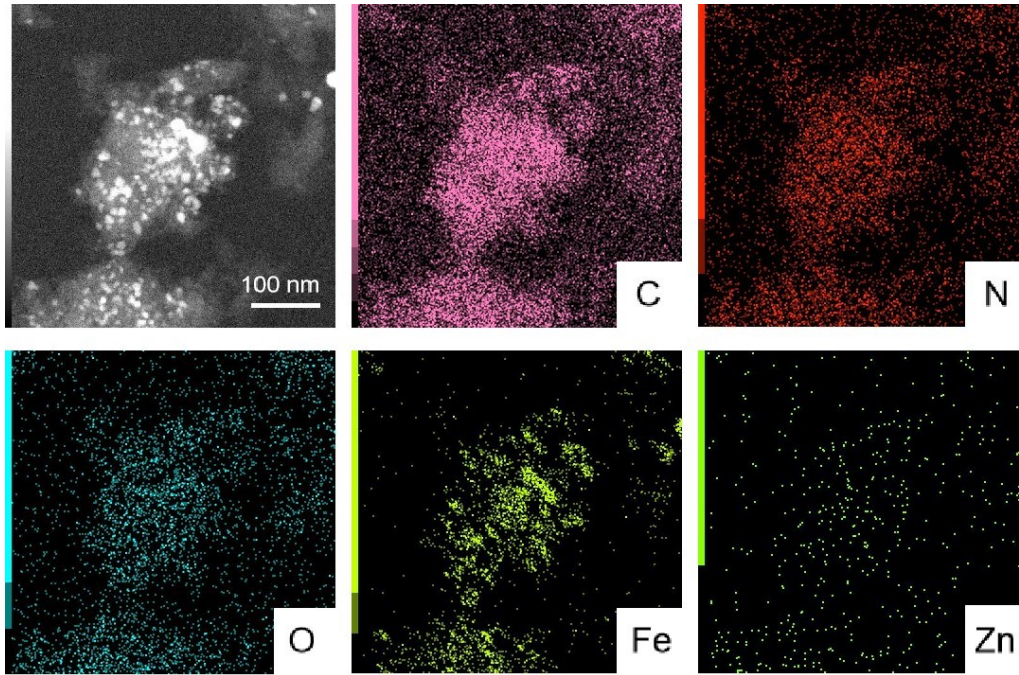


Fig. S3. STEM and corresponding elemental mapping images of Fe(25)Zn@NC-m.

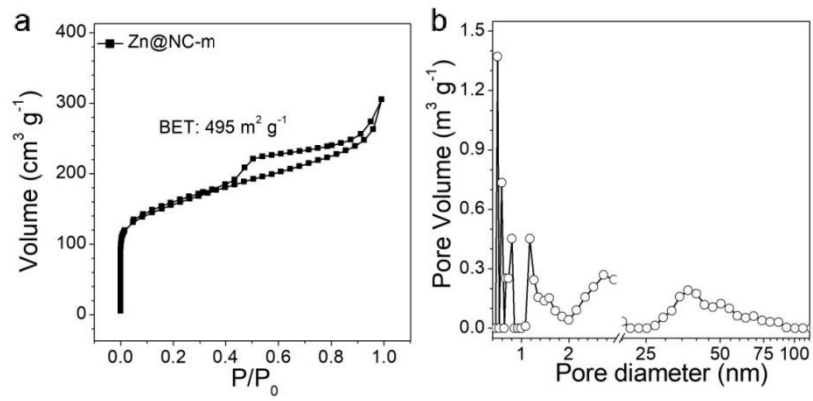


Fig. S4. (a) N_2 adsorption–desorption isotherm and (b) pore size distribution of Zn@NC-m.

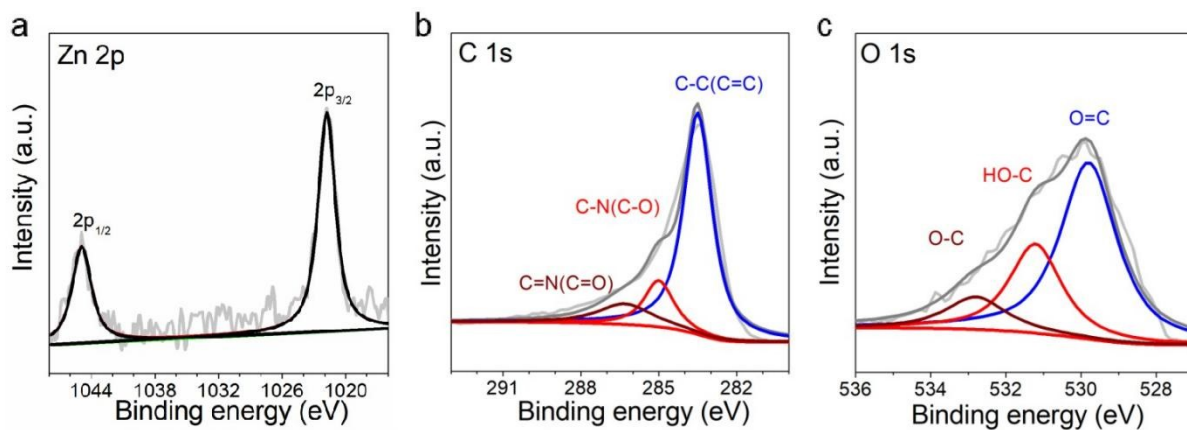


Fig. S5. High-resolution (a) Zn 2p, (b) C 1s, and (c) O 1s XPS spectra of Fe(25)Zn@NC-m.

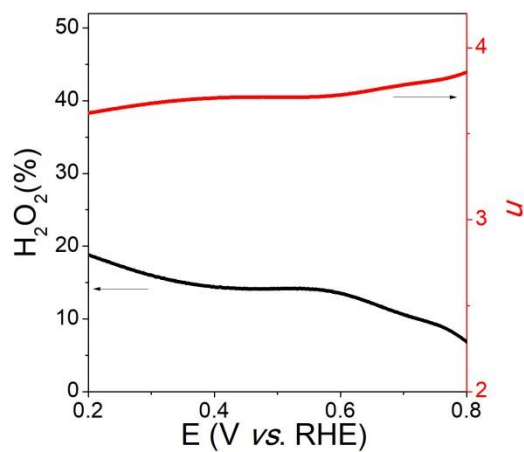


Fig. S6. H_2O_2 yield and electron transfer number of Fe(25)Zn@NC-m.

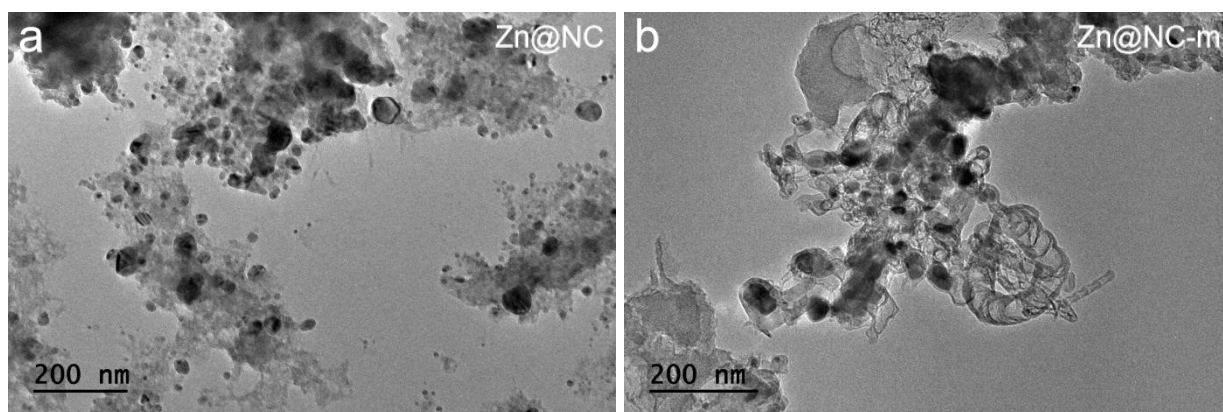


Fig. S7. TEM image of (a) Zn@NC and (b) Zn@NC-m.

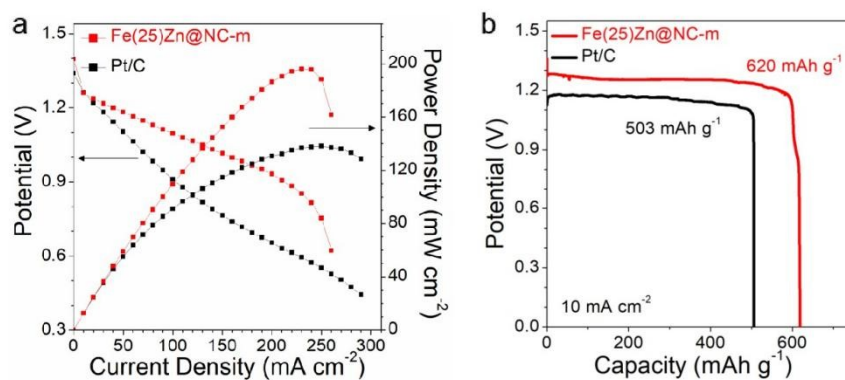


Fig. S8. (a) Discharge polarization and power density curves of primary Zn-air battery using Fe(25)Zn@NC-m and Pt/C. (b) Specific capacities of primary Zn-air battery.

Table S1. Comparison of ORR catalytic performances of reported Fe-containing catalysts in 0.1 M KOH solution.

Catalysts	$E_{1/2}$ [V]	Reference
Fe(25)Zn@NC-m	0.868	This work
Fe ₁ /N-HCMs	0.88	<i>Small</i> , 2023 , 19, 2207991.
NiFe-LDH/Fe ₁ -N-C	0.90	<i>Adv. Energy Mater.</i> , 2023 , 13, 2203609.
Fe-N-C HSs	0.90	<i>Small</i> , 2023 , 2305700
FeCu-SAC	0.926	<i>J. Mater. Chem. A</i> , 2023 , 11, 6191-6197.
Mn-Fe@NCNTs	0.872	<i>J. Alloys Compd.</i> , 2023 , 953, 169992.
Fe/Fe ₃ C@C	0.831	<i>Electrochem. Commun.</i> , 2023 , 150, 107477.
Fe-NC-Gs	0.85	<i>Electron. Mater. Lett.</i> , 2023 , 285.
Po-FeCo-N-C	0.83	<i>Materials Science and Engineering B</i> , 2023 , 290, 116291.