

Supporting Information:

Hierarchical 3D Porous Carbon with Facilely Accessible Fe-N₄ Single-Atom Sites for Zn-Air Batteries

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1. Experimental Section

1.1. Chemicals and materials

All chemical reagents were employed without further treatment. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Sinopharm Chem. reagent Co. Ltd, China), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (98%, Sinopharm Chem. reagent Co. Ltd, China), methanol (99.5%, Aldrich Industrial Co.), ammonia solution (28~30%, Sinopharm Chem. reagent Co. Ltd, China), 2-methylimidazole (98%, Aldrich Industrial Co.), Nafion (5 wt%). Tetraethyl orthosilicate (25%, Sigma Aldrich.).

1.2. Catalysts synthesis

1.2.1. Synthesis of silica nanosphere

Silica nanospheres employed as templates were synthesized by a modified Stöber method.¹ Typically, tetraethyl orthosilicate (15 mL) was dropwise added to a mixture of ammonia solution (28~30%, 5 mL), ethanol (225 mL) and deionized water (30 mL). After 2 hours of continuous stirring, silica spheres were obtained by centrifugation, washing and vacuum drying overnight.

1.2.2. Synthesis of SA-Fe-3DOMC

Silica nanospheres (0.5 g), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.87 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (25 mg) were firstly dispersed in 20 mL of methanol anhydrous. Subsequently, 1.0 g of 2-methylimidazole was dissolved in 20 mL of methanol anhydrous in another beaker. Next, the two above solutions were rapidly mixed together and heated at 60 °C for 24 h. The obtained $\text{SiO}_2@\text{ZIF-8-Fe}$ nanocomposites were pyrolyzed at 900 °C for 2 h under Ar atmosphere with a ramp of 2 °C min^{-1} . Finally, the SA-Fe-3DOMC catalyst was obtained by HF leaching (8%, 40 mL) for 12 hours and a second heat-treatment in Ar for 1 hour at 900 °C. For comparison, the contrast samples were prepared under

conditions similar to that used for SA-Fe-3DOMC. NC was synthesized without ferric chloride, and Fe-N-C was synthesized with 50 mg ferric chloride by the same method.

1.3. Characterization of samples

The morphologies of the prepared samples were observed by SEM (Phenom) and TEM (TEM, JEM2010F). HAADF-STEM image and EDS elemental mapping were also performed on FEI Tecnai. The structure of single Fe atoms was observed by Aberration-corrected HAADF-STEM (JEM-ARM300F). XRD were characterized on a Bruker D8 Advance A25X using Cu K α radiation. The Raman spectra were analyzed on Laser confocal instrument (Renishaw Invia). Nitrogen adsorption-desorption isotherms were performed on KuboX-1000, the pore size distribution in N₂ sorption isotherms were derived from the adsorption branch of the isotherm. Inductively coupled plasma mass spectrometry (ICP-MS) were conducted on Agilent 720ES, and X-ray photoelectron spectroscopy (XPS) results were obtained with a Thermo Fisher Scientific, Escalab 250Xi with Al K α radiation.

2. Electrochemical tests

All the electrochemical measurements were performed using conventional three-electrode system. MSR electrode rotator (Versa STAT 3, Princeton Research, USA electrochemical workstation.) was used to carry out the rotating disk electrode (RDE). Potentiostat/Galvanostat (Versa STAT 3, Princeton Research, USA electrochemical workstation) was used to record. Carbon rod and Hg/HgO electrode (1 M KOH solution) were used as counter electrode and reference electrode, respectively. RDE with diameters of 5.0 mm were used as the working electrodes. First, 5 mg of the catalyst was dispersed in a mixed solution containing 190 μ L of deionized water, 760 μ L of isopropanol, and 50 μ L of a 5 wt% Nafion solution. To obtain a well-dispersed ink, the above mixed solution needed to

be sonicated for at least 2 h. The catalyst ink (20 μL) was then dropped evenly on the surface of the glassy carbon electrode in portions and dried at room temperature. The loading of the as-prepared catalyst is 0.5 mg cm^{-2} . For comparison, the loading of commercial 20 wt% Pt/C on the glassy carbon electrode is $25 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$. Cyclic voltammetry (CV) curves were measured in 0.1 M KOH solutions saturated with N_2 and O_2 , respectively.² The measured potential was between 0.05 and 1.2 V, and the scan rate was 10 mV s^{-1} . The RED experiments were performed in O_2 saturated 0.1 M KOH, and different speeds were measured with a scan rate of 10 mV s^{-1} . By performing CV 10,000 cycles in the 0.6-1.0 V range, the accelerated durability test (ADT) was performed at a sweep speed of 100 mV s^{-1} .

The K-L equations can be used to analyze kinetic parameters as following:^{3,4}

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

$$B = 0.2nF(D_0)^{2/3}v^{-1/6}C_0 \quad (2)$$

Where j represents the measured current density, ω is the electrode rotating rate, F is the Faraday constant (96485 C mol^{-1}), j_k is the kinetic current density, C_0 is the bulk concentration of O_2 0.1 M KOH ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$), D_0 is the oxygen diffusion coefficient ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) of 0.1 M KOH, and v is the kinematic viscosity of 0.1 M KOH ($0.01 \text{ cm}^2 \text{ s}^{-1}$). As for the RRDE measurements, the potential on the disk electrode was scanned from 1.15 to 0.05V (vs. RHE) with a rate of 10 mV s^{-1} , while the ring-electrode potential was set at 1.3 V (vs. RHE). The H_2O_2 production percentage and the electron transfer number (n) were obtained from the following equations:

$$\text{H}_2\text{O}_2(\%) = 200 \frac{I_r/N}{I_d + I_r/N} \quad (3)$$

$$n = 4 \frac{I_d}{I_d + I_r/N} \quad (4)$$

where I_d and I_r are the disk current and the ring current, respectively, and N is the current collection efficiency. and N means the current collection efficiency (0.37) of the Pt ring.

3. Zn-air battery tests.

For battery tests, a polished Zinc plate was used as the anode, carbon paper loaded with the SA-Fe-3DOMC catalyst was the air cathode and a mixture of 6 M KOH and 0.2 M $Zn(CH_3COO)_2$ was the electrolyte.⁵⁻⁷ 6 mg of catalyst was dispersed into 1100 μL ethanol and 100 μL 5% Nafion aqueous solution followed by ultrasonic treatment for 30 min to prepare the catalyst ink. 400 μL of the prepared catalyst ink was loaded on 1 cm^2 carbon paper and natural drying (loading amount of 2.0 mg cm^{-2}). A control sample is also prepared by adding 3 mg Pt/C into 1170 μL ethanol and 30 μL 5% Nafion aqueous solution (loading amount of 1.0 mg cm^{-2}). The discharge polarization curves were obtained on a potentiostat/galvanostat (Versa STAT 3, Princeton Research, USA electrochemical workstation). The discharge curves at different currents and galvanostatic discharge stability were obtained on Bio-logic SP-150 electrochemical workstation.

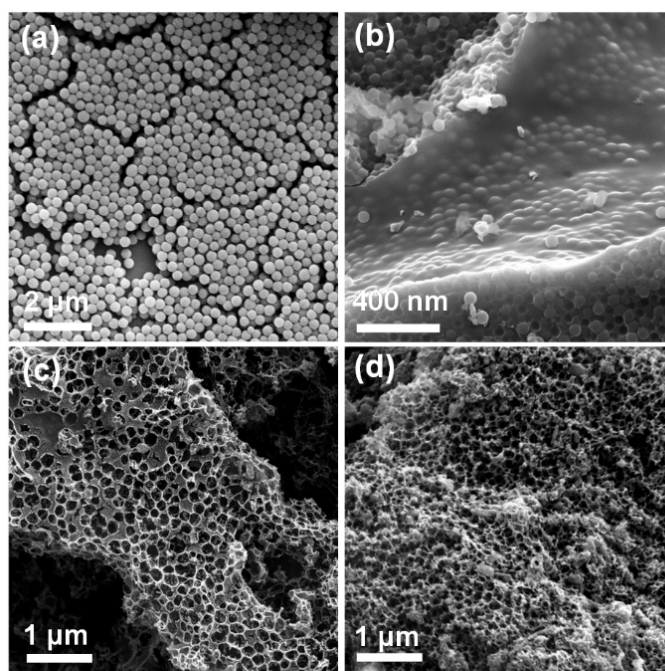


Fig. S1 (a) SEM images of silicon spheres, (b) ZIF-8-Fe grown in situ on the surface of silicon spheres, (c) N-C and (d) Fe-N-C-50.

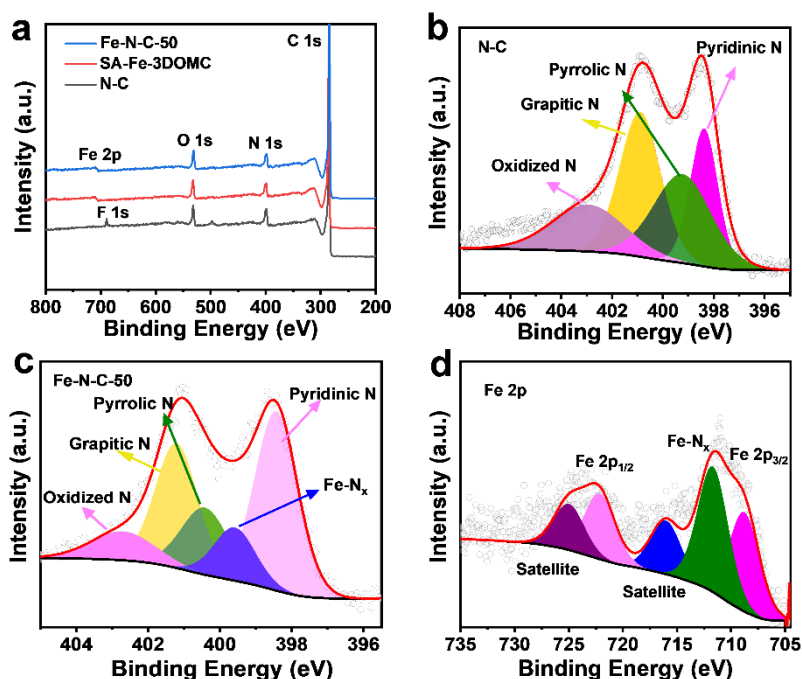


Fig. S2 (a) XPS spectra Survey scan of N-C, SA-Fe-3DOMC and Fe-N-C-50, (b, c) N 1s high resolution XPS spectra of N-C and Fe-N-C-50. (d) Fe 2p high resolution XPS spectra of Fe-N-C-50.

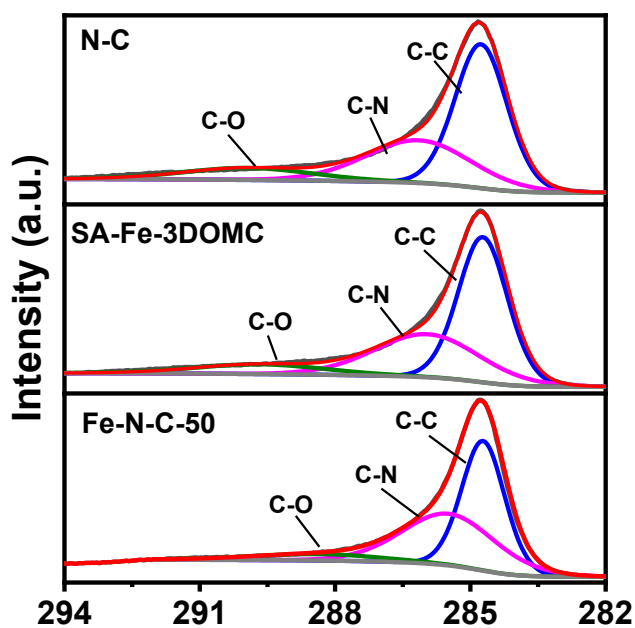


Fig. S3 C 1s high resolution XPS spectra of N-C, SA-Fe-3DOMC and Fe-N-C-50.

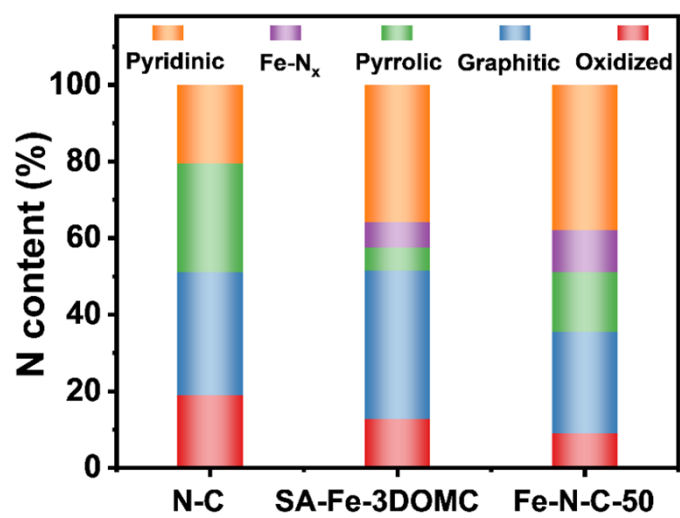


Fig. S4 Relative content of different N species of N-C, SA-Fe-3DOMC and Fe-N-C-50.

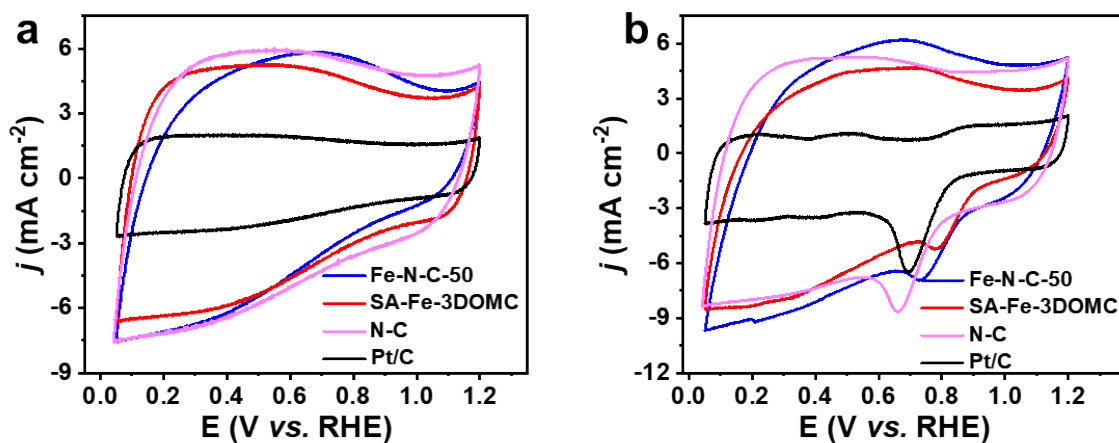


Fig. S5 CV curves of Pt/C, N-C, SA-Fe-3DOMC and Fe-N-C-50 measured at the same scan speed (10 mV s^{-1}) of ORR in (a) N₂ and (b) O₂ saturated 0.1 M KOH solution.

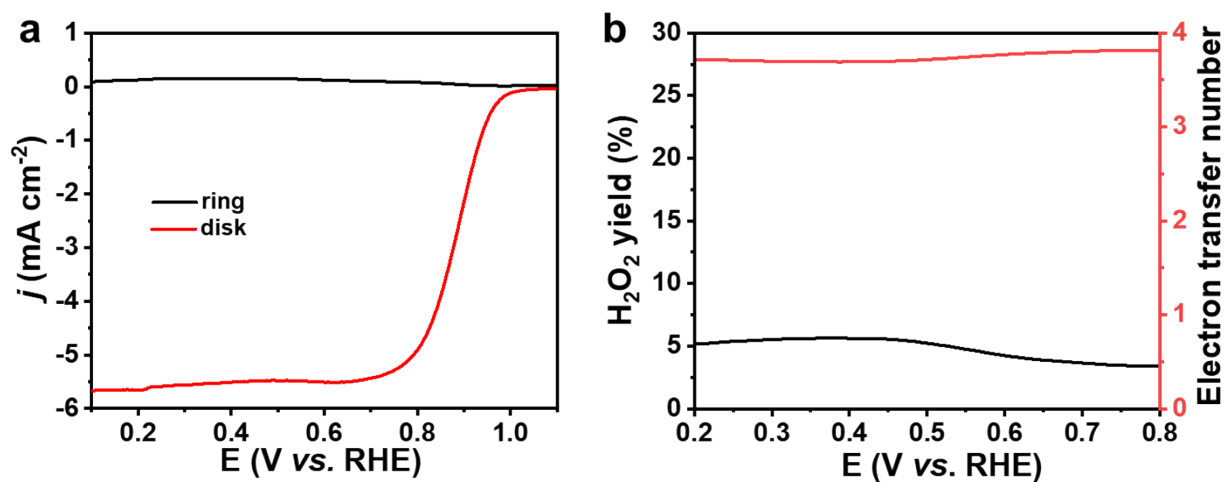


Fig. S6 (a) RRDE voltammograms and (b) the calculated electron transfer numbers and H₂O₂ yields of SA-Fe-3DOMC catalyst.

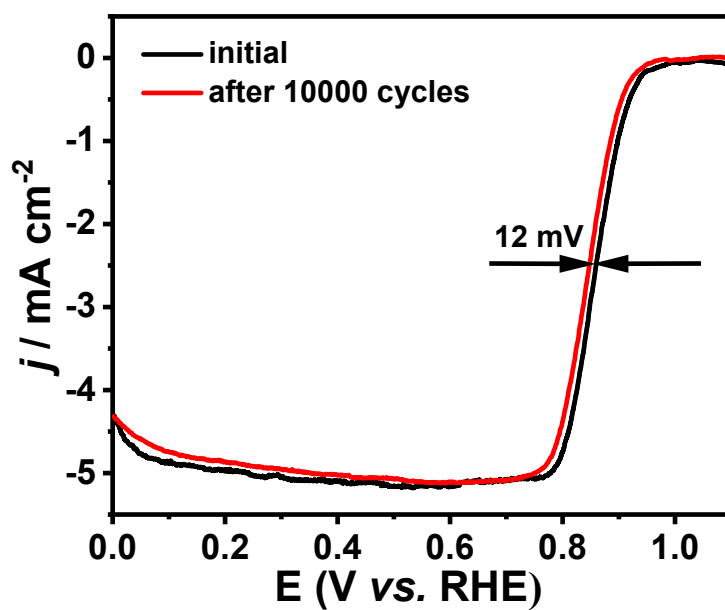


Fig. S7 ORR LSV curves of 20 wt% Pt/C initially and after 10,000 cycles between 0.6 and 1.0 V at a scan rate of 100 mV s^{-1} .

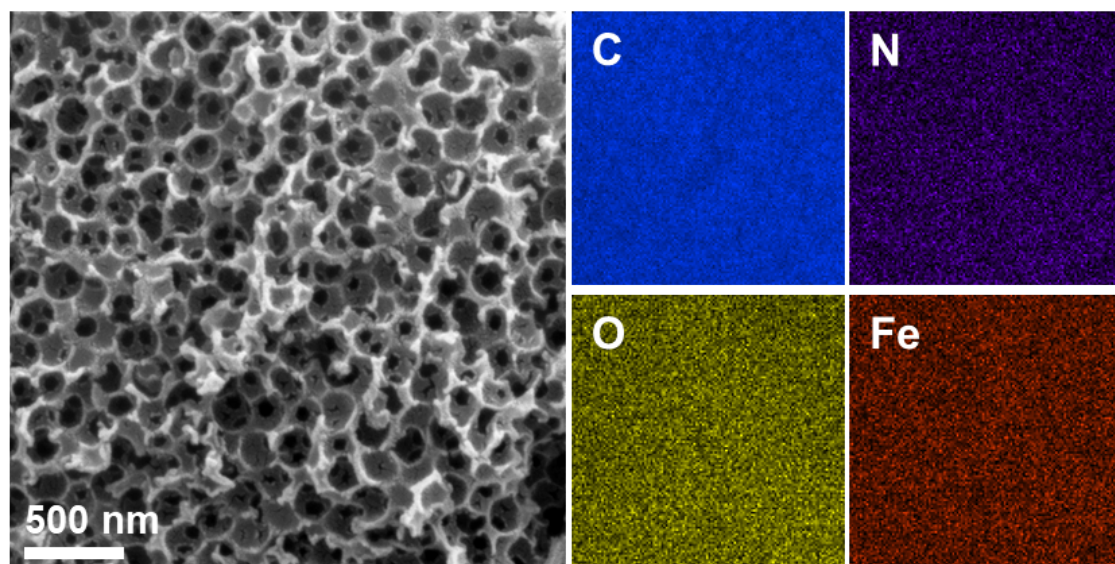


Fig. S8 SEM image of SA-Fe-3DOMC after 10,000 potential cycles and corresponding elemental images.

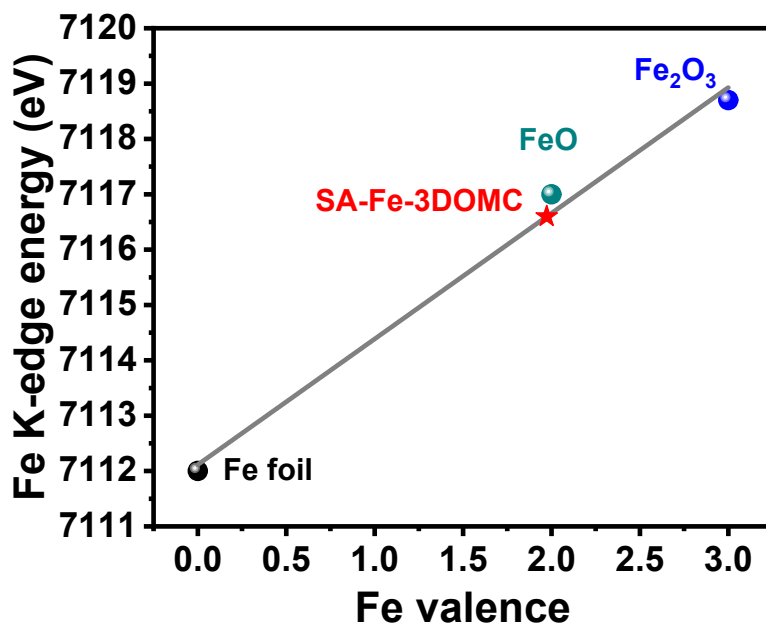


Fig. S9 Linear fitting curve of SA-Fe-3DOMC and reference materials derived from corresponding Fe K-edge XANES spectra.

Table S1. Fe K-edge EXAFS fitting results.

Sample	Path	N	$R(\text{\AA})$	$\sigma^2(\times 10^{-3} \text{\AA}^2)$	ΔE_0 (eV)	R factor
SA-Fe-3DOMC	Fe-N	4.178	2.006	7.45	-3.262	0.020

[a]: k range: 2-11.0 (\AA^{-1}); R range: 1-2 \AA ; $S_0^2 = 0.8335$ was determined from the Fe foil and used for Fe K-edge fitting.

References

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