

Supporting Information

Rational design and synthesis of hollow Fe–N/C electrocatalysts for enhanced oxygen reduction reaction

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1. Experimental Section

1.1 Catalyst preparation

The synthetic method of Hollow Fe-N/C-800 material is as follows. 0.4 g of resorcinol was dissolved in 70 mL of ethanol with 10 mL of distilled water. Later, 3 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ was injected to adjust pH value to 8–9. Then, 0.56 mL of methanol (CH_2O) was added to activate polymerization. Tetraethyl orthosilicate (TEOS) was used as the template agent, and 2.8 mL of TEOS was added to the above solution. At the same time, the Fe-precursor solution was added to the above solution and stirred for 6 h at room temperature to form red Fe@phenolic resin@ SiO_2 (Fe-RF- SiO_2) precursor. Fe-precursor solution was prepared by 0.79 g of 1,10-Phenanthroline (Phen) mixing with 0.36 g of FeSO_4 (Fe) in 10 mL of 50% ethanol water. Afterwards, the Fe-RF- SiO_2 material was pyrolyzed at 800 °C for 2 h under N_2 atmosphere to obtain the Fe-N/C-800 @ SiO_2 materials. Finally, the Hollow Fe-N/C-800 material was obtained by etching SiO_2 of Fe-N/C-800 @ SiO_2 in 6 mol L^{-1} KOH solution for more than 6 h.

For comparison, the Solid Fe-N/C-800 and Hollow N/C-800 were also prepared. The Solid Fe-N/C catalyst was prepared under the same condition as the Hollow Fe-N/C-800 only without adding TEOS as template agent. The Hollow N/C-800 was obtained under the same condition as the Hollow Fe-N/C-800 only without adding Fe-precursor solution.

1.2 Material characterization

The morphology of the prepared samples was characterized with field emission scanning electron microscopy (FE-SEM, JEOL JSM- 7001F), transmission electron microscopy (TEM, FEI TF20) and atomic force microscope (AFM, Bruker Dimension Fastscan). Specific surface areas of these as-prepared samples were calculated using Brunauer-Emmett-Teller (BET) method (ASAP 2020m, Micromeritics, USA). The pore size distribution was obtained by Barrett-Joyner-Halenda (BJH) method using adsorption branch of the nitrogen isotherm. Raman spectroscopic analysis was

performed with a Labram-010 Raman micro-spectroscopy (JY, FRA) system utilizing a 514.5 nm incident radiation in the range from 400 cm⁻¹ to 2000 cm⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ESCALAB250 XPS spectrometer. ICP-AES measurement results were relying on Agilent 720ES equipment^[3]. Elemental mapping was conducted using EDAX detector attached on JEM-2100F. The surface oxidation states were analyzed using Fourier transform infrared spectrometer (FTIR, Tensor 27, 500-4000 cm⁻¹)

1.3 Electrochemical measurements:

1.3.1 RDE measurement

Electrochemical measurements were performed using a CHI Electrochemical Station (760 D) in a standard three-electrode system. A rotating disk electrode (RDE) equips a glassy carbon electrode with diameter of 0.5 cm sheet, a platinum electrode sheet, and a saturated calomel electrode (SCE) were used as working electrode, counter electrode, and reference electrode, respectively. The catalyst ink was prepared by ultrasonically dispersing 1 mg of catalyst in 1 mL of water and 20 µL of binding agent. Later, 15 µL of catalyst ink was coated on the surface of a glassy carbon electrode, yielding a catalyst loading of 0.1 mg cm⁻². All electrochemical tests were performed at room temperature in 0.1 M KOH or 0.5 M PBS, which was bubbled with O₂ or N₂ for 30 min and maintained at the same atmosphere during the measurements. A potential at which the current density exceeded a threshold value of 0.1 mA cm⁻² was the onset potential (E_{onset}), and the potential corresponding to 50% of the diffusion-limited current density was defined as the half-wave potential ($E_{1/2}$). The electron transfer numbers (n) of ORR at various potentials on the samples were calculated by the Koutecky-Levich equation:

$$j^{-1} = j_k^{-1} + (0.62nFAD^{2/5} V^{-1/6} C)^{-1} \omega^{-1/2} \quad [1]$$

where j is the measured current density, j_k is the kinetic limiting current density, F is Faraday constant (96500 C mol⁻¹), C_0 is the bulk concentration of oxygen, D_0 is the diffusion co-efficient of oxygen in the bulk solution, ν is the kinematic viscosity ($\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$), and ω is the angular velocity of the disk ($\omega = 2\pi N$, N is the linear

rotation speed). In 0.1 M KOH solution: $C_0 = 2.4 \times 10^{-3} \text{ mol L}^{-1}$, $D_0 = 2.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. In 0.5 M PBS solution: $C_0 = 2.6 \times 10^{-3} \text{ mol L}^{-1}$, $D_0 = 2.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

1.3.2 RRDE measurement

For the RRDE measurements, catalyst inks and electrodes were prepared by the same method as for RDE. The disk electrode was scanned at a rate of 5 mV s^{-1} , and the ring potential was constant at 0.46 V versus SCE. The percentage of HO_2^- intermediate production ($\% \text{ HO}_2^-$) and electron transfer number (n) were determined by the followed equations.

$$\% \text{ HO}_2^- = \frac{200I_r}{NI_d + I_r} \quad n = \frac{4NI_d}{NI_d + I_r} \quad [2]$$

where I_d is the disk current, I_r is the ring current, and N is the current collection efficiency of the Pt ring, which was determined to be 0.28.

1.4 Construction and operation of the microbial fuel cells and zinc-air cells

1.4.1 MFCs preparation

A single-chamber air-cathode MFCs device of volume of 28 mL was used. And the corresponding details in assembling the MFCs was referred to the references.^[1] In the operational stage, the output voltage of those MFCs were collected by 16 channel data acquisition system (MPS 010602, Beijing).^[2] Moreover, the polarization curves of different cathode were acquired by adjusting the external circuit resistance from 40Ω to 5000Ω , and anode electrode potentials were measured by inserting a saturated calomel electrode (SCE) electrode to compose two-electrode system. By means of formula $P = V \times I$, the power density P can be easily calculated. Both I and P were normalized to the efficient area of cathode surface, and current density I was calculated using the formula of $I = V (\text{cell voltage}) / (R \times A)$ (external resistance and efficient area).

1.4.2 Zn-air battery test

The air electrodes were prepared by uniformly casting the catalyst ink on commercial Teflon-coated carbon fiber paper (SGL carbon paper, Germany). The catalyst ink was prepared as same as the MFCs. The battery was assembled using a

zinc foil as the anode and 6 mol L⁻¹ KOH with 1.2 g zinc acetate solution as the electrolyte. The battery was equipped with a pump to circulate the electrolyte during the test. The galvanostatic discharge test was carried out using a CHI Electrochemical Station (760 D) at room temperature. To assess the cathode performance, the step current method experiment was carried out using the electrochemical workstation at different current densities.

1.4.3 Chemical oxygen consumption (COD) analysis

The chemical oxygen consumption was performed by Ammonia nitrogen detector (5B-3C V8). The digestion of water was also processed by the digestion instrument. The water sample, which was taken from the MFCs equipment, was experienced a pretreatment process. Firstly, the exact amount of 2.5 mL distilled water was added to a reaction tube as blank. Each water sample of 2.5 mL was accurately taken and added to other reaction tube. 0.7 mL special consumable D reagent was added to each reaction tube and 4.8 mL of special consumable E reagents were added in turn. Then the reaction solutions were fully mixed by shaking. Later, each reaction tube was put into the digestion tank in order to eliminate the program. After the digestion was completed and cooled, 2.5 mL distilled water was added to each reaction tube successively, and then the cuvettes were imported with digestion solution. Finally, the COD data was read by using the standard curve.

1.5 References

- [1] X. T. Wu, J. C. Li, Q. R. Pan, N. Li, Z. Q. Liu, *Dalt. Trans.*, **2018**, 47, 1442–1450.
- [2] L. Tan, N. Li, S. Chen, Z.-Q. Liu, *J. Mater. Chem. A*, **2016**, 4, 12273–12280.
- [3] H. Ren, Y. Wang, L. Zhuang, et al. *J. Energy Chem.*, **2017**, 4, 616–621.

2. Supplementary Figures

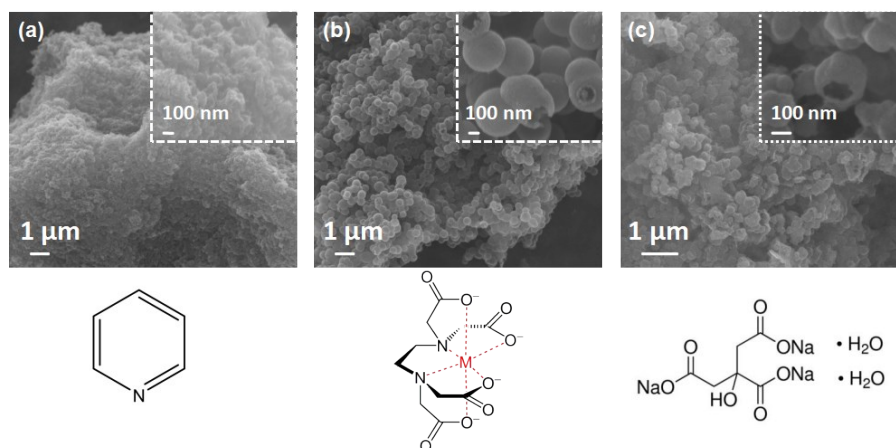


Figure S1. SEM images of as-prepared materials in various chelating agents: (a) pydin; (b) EDTA; (c) sodium citrate.

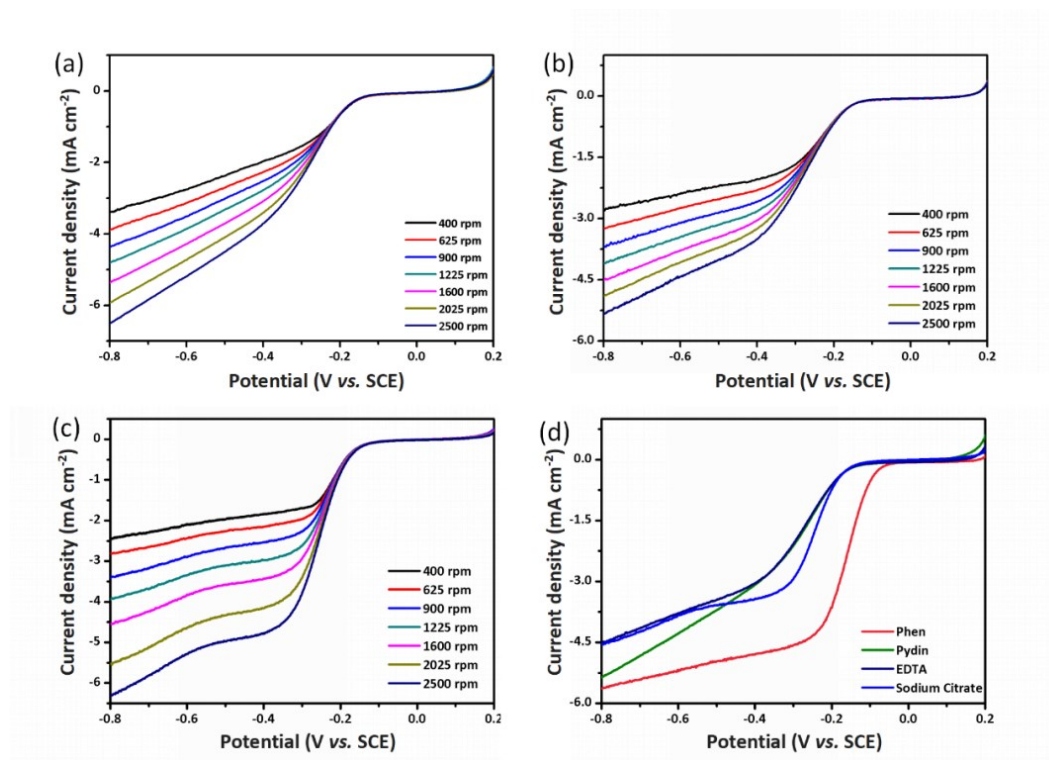


Figure S2. LSV curves of as-prepared materials in various chelating agent, (a) pydin; (b) EDTA; (c) sodium citrate; (d) general LSV curves among four kinds of complexant in O_2 -saturated alkine

solution under 1600 rpm.

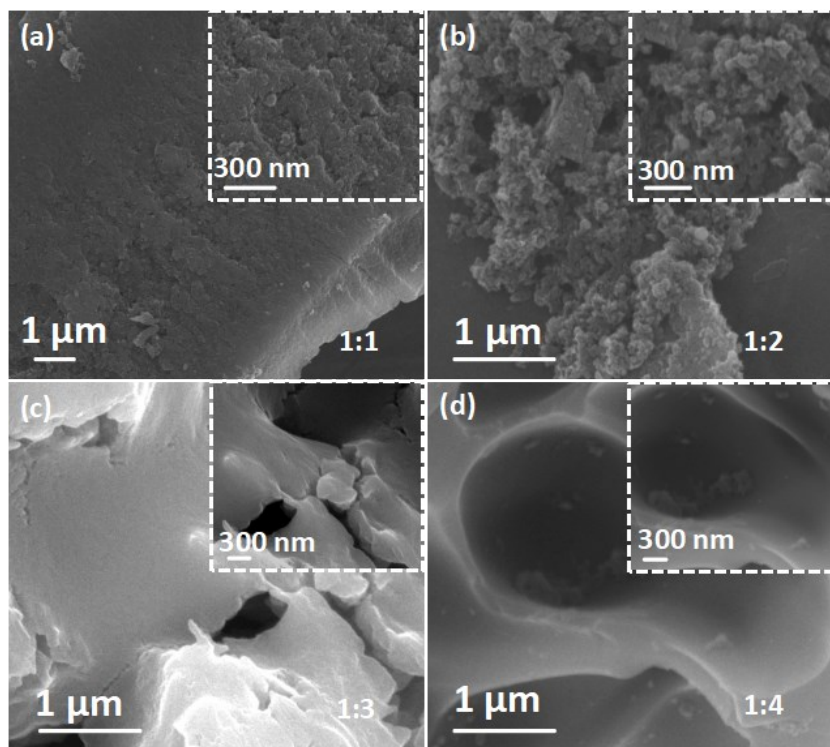


Figure S3. SEM images of as-prepared materials with different ratios of Fe^{2+} : Phen: (a) 1:1; (b) 1:2; (c) 1:3; (d) 1:4.

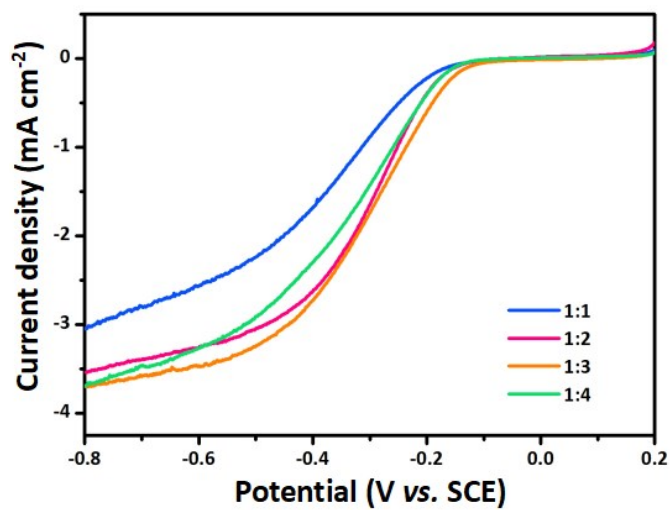


Figure S4. LSV curves of as-prepared materials with different ratio of Fe^{2+} : Phen.

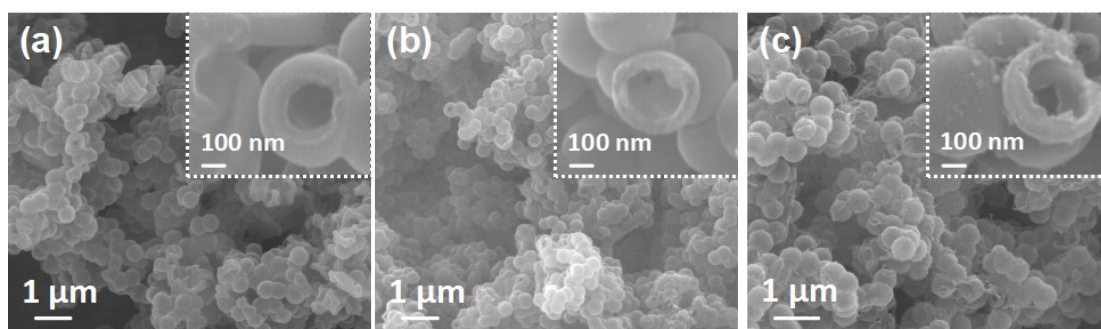


Figure S5. (a-c) SEM images of as-prepared materials in various heat-treatment temperatures: (a) 700 °C; (b) 800 °C; (c) 900 °C.

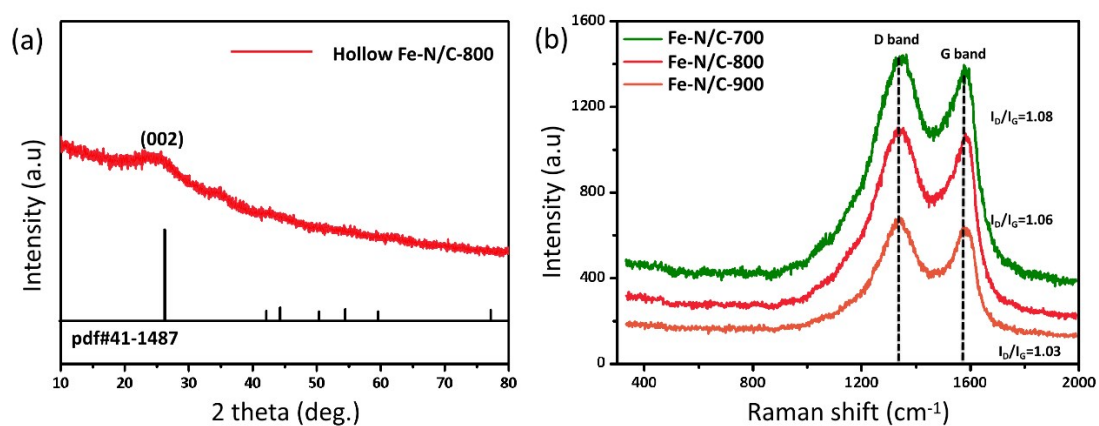


Figure S6. (a) XRD pattern of Hollow Fe-N/C-800 and (b) the Raman patterns of samples under several temperature.

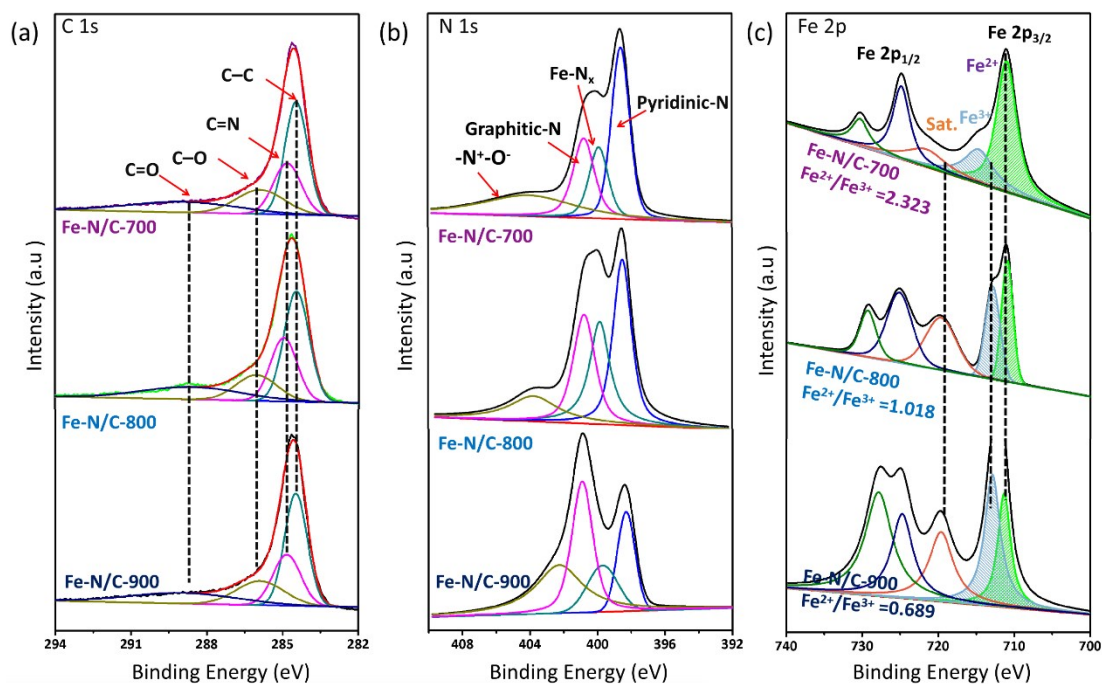


Figure S7. XPS narrowband distributed patterns of various temperature of as-prepared (n (Reso): n (Phen): n (Fe³⁺) = 1:3:1) (a) C 1s; (b) N1s; (c) Fe 2p.

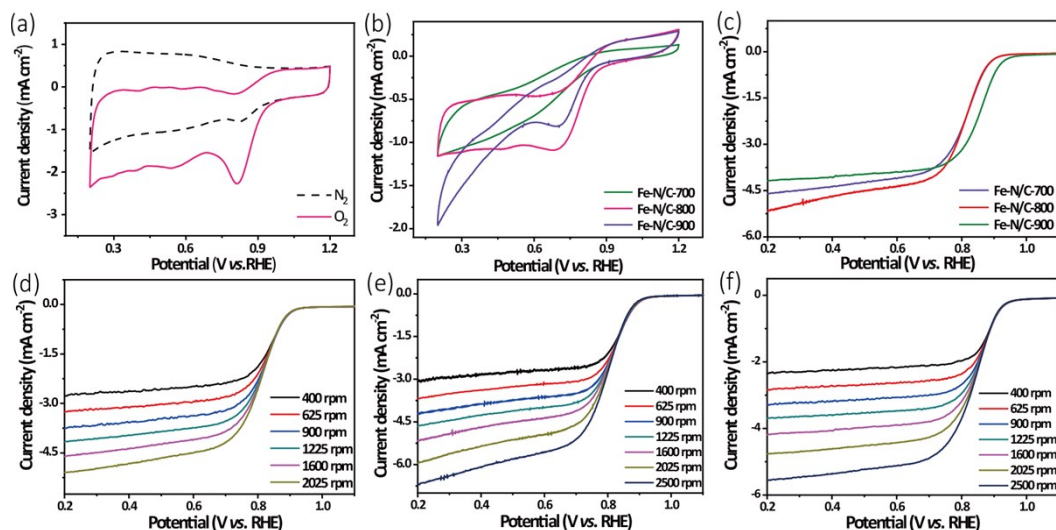


Figure S8. (a) CV patterns of Fe-N/C-800 in saturated-O₂/N₂; (b) CV patterns of Fe-N/C-X in saturated O₂; (c) LSV curves of Fe-N/C-X in 0.1 M KOH with saturated O₂; (d-f) LSV curves for various rotate speeds of Fe-N/C-700, Fe-N/C-800 and Fe-N/C-900, respectively.

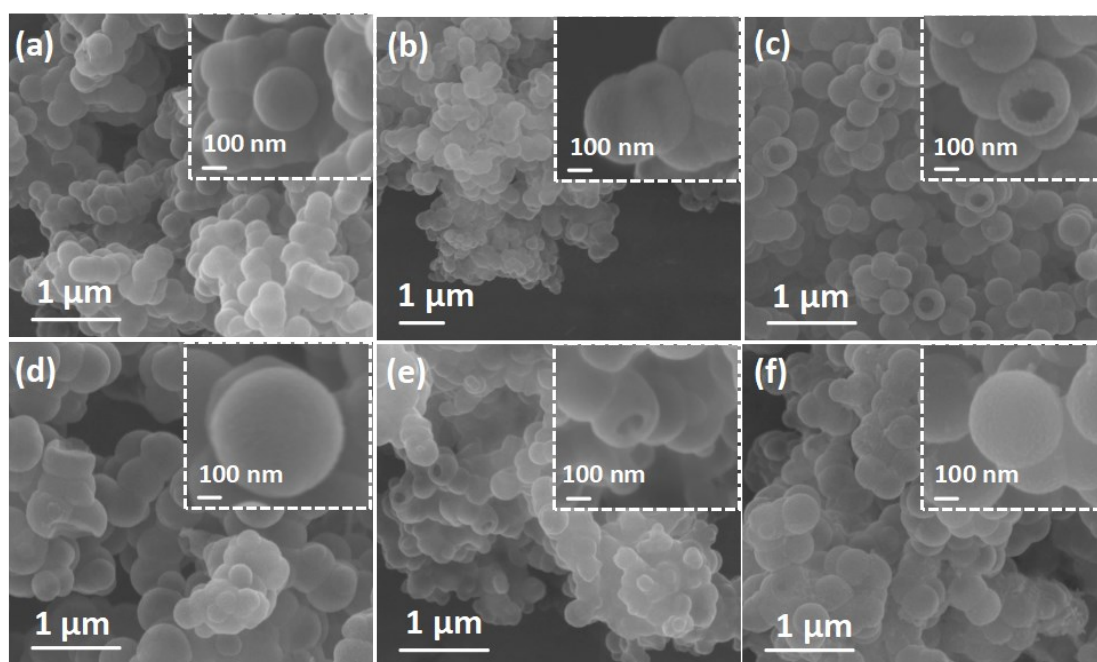


Figure S9. SEM images of as-prepared materials in various ratio of Reso to Phen: (a) 1:2; (b) 1:3; (c) 1:1; (d) 2:1; (e) 3:1; (f) 4:1.

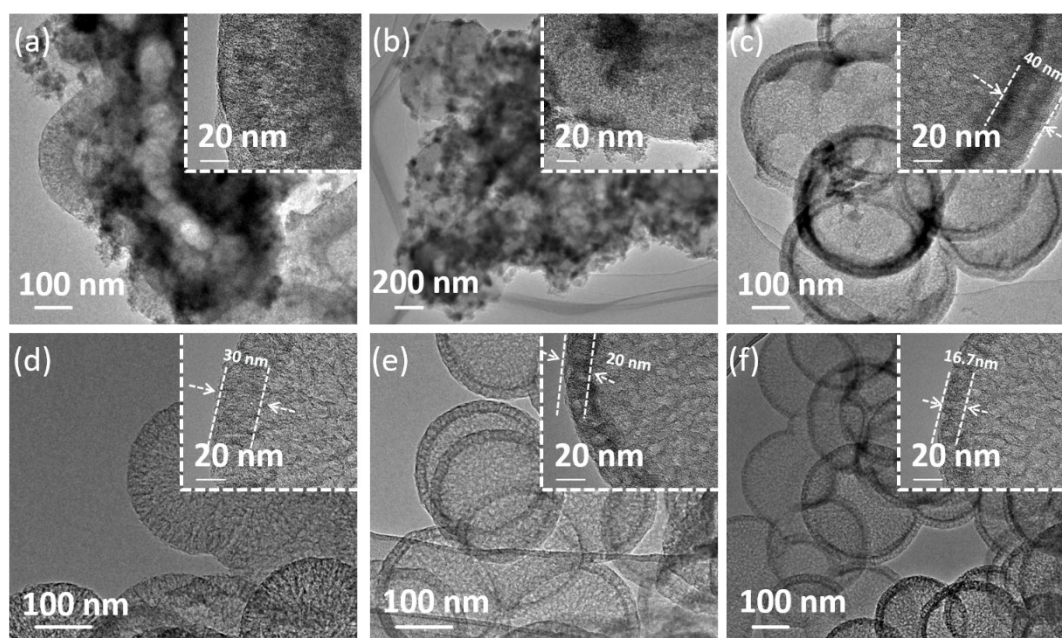


Figure S10. TEM and HRTEM images of as-prepared materials in various ratio of Reso to Phen: (a) 1:2; (b) 1:3; (c) 1:1; (d) 2:1; (e) 3:1; (f) 4:1.

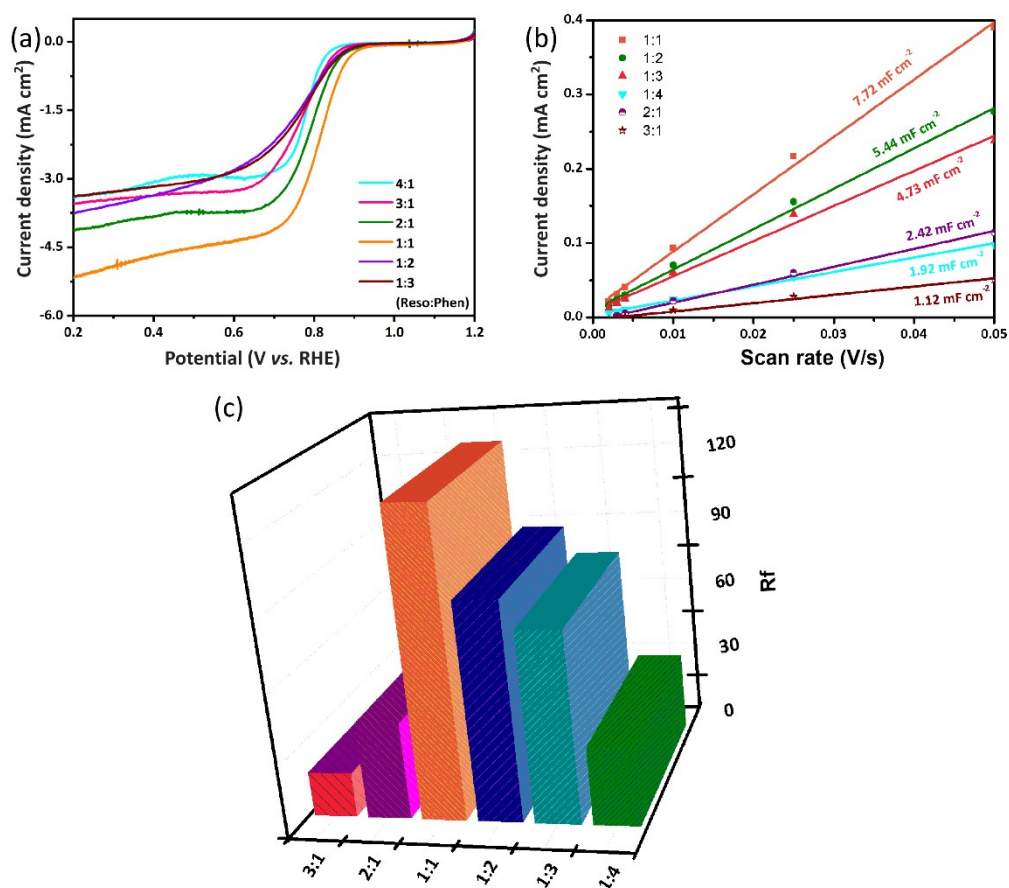


Figure S11. (a) LSV curves of Fe/N-CNFs catalysts prepared with different ratios of Reso: Phen; (b) the C_{dl} curves of materials and (c) the ECSA.

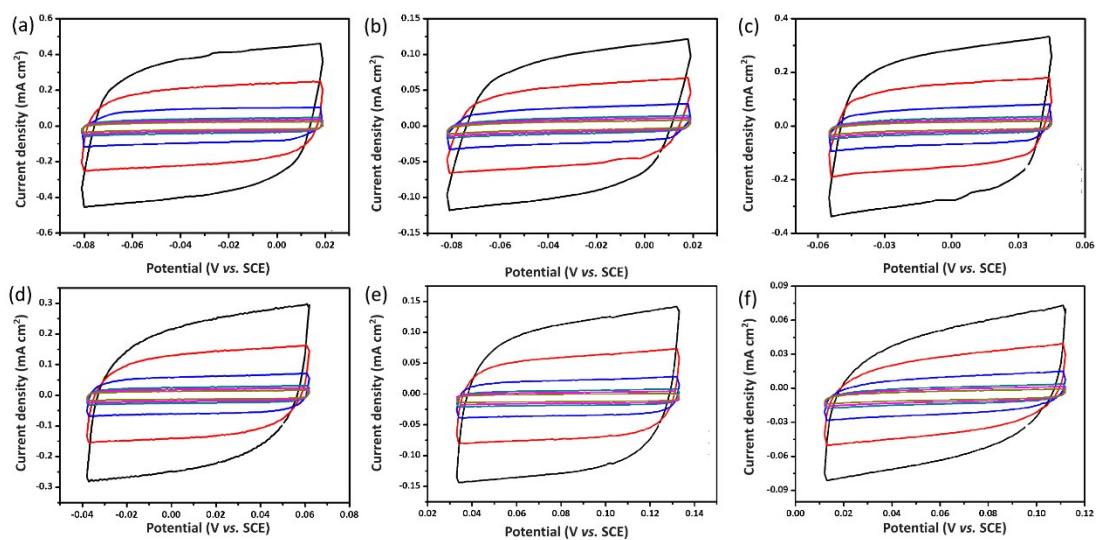


Figure S12. The CV curves of different scan rates (50/25/10/4/3/2 mV dec⁻¹) of various catalysts (Reso: Phen). (a) 1:4; (b) 1:3; (c) 1:2; (d) 1:1; (e) 1:2; (f) 1:3.

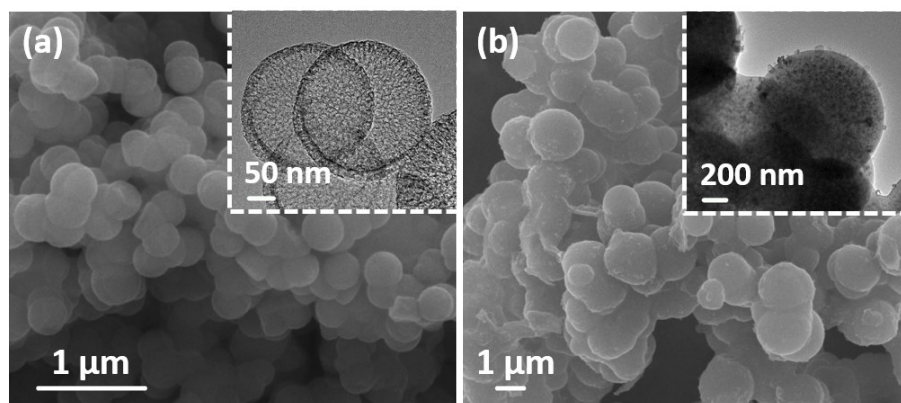


Figure S13. SEM images of different kind of catalysts (a) Hollow N/C-800; (b) Solid Fe-N/C-800.

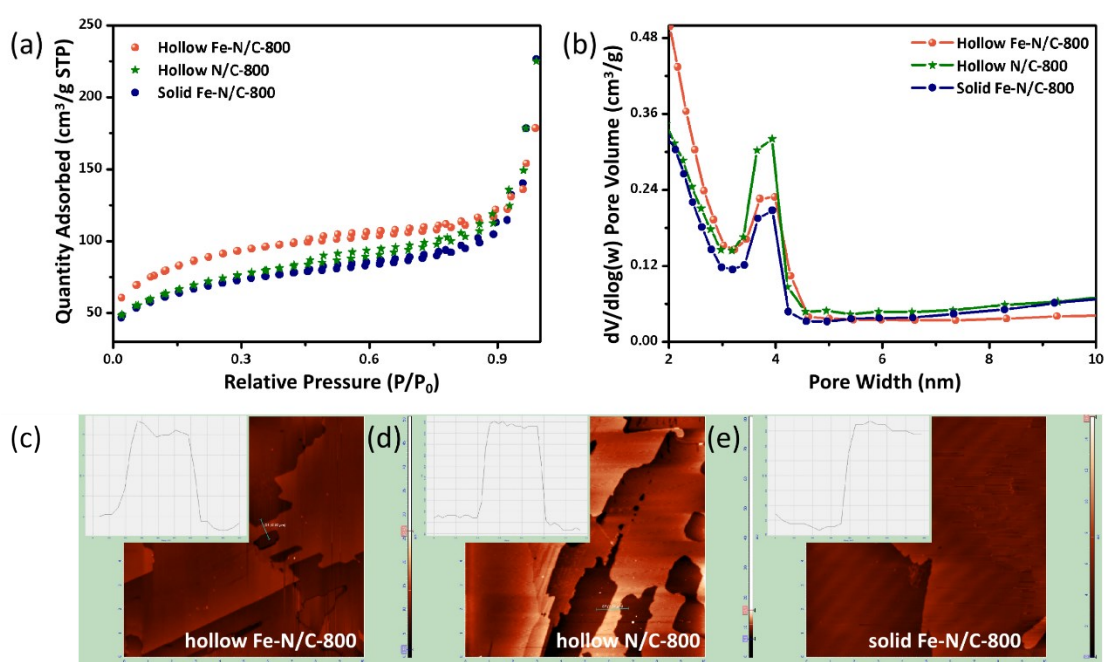


Figure S14. (a) BET Isotherm Linear Plot of samples; (b) BJH Desorption $dV/d\log(w)$ Pore Volume; (c-e) AFM images of the Hollow Fe-N/C-800, Hollow N/C-800 and Solid Fe-N/C-800, respectively.

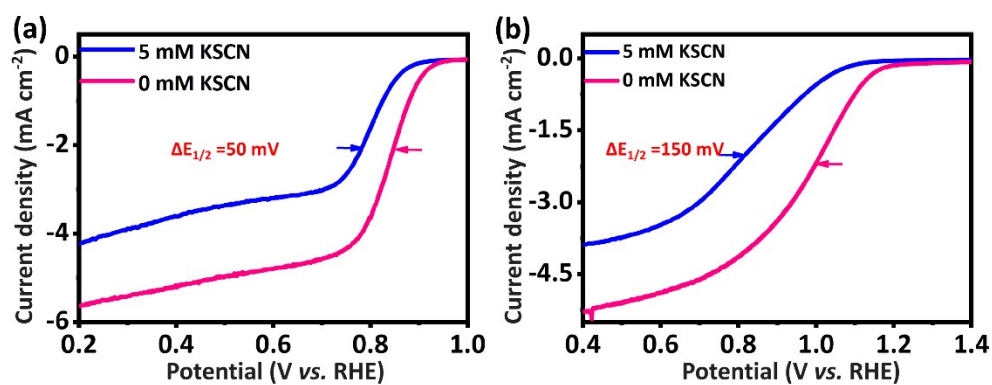


Figure S15.(a-b) Effects of SCN^- ions on ORR activities of the Hollow Fe-N/C-800 catalyst in 0.1 M KOH and PBS electrolyte, respectively.

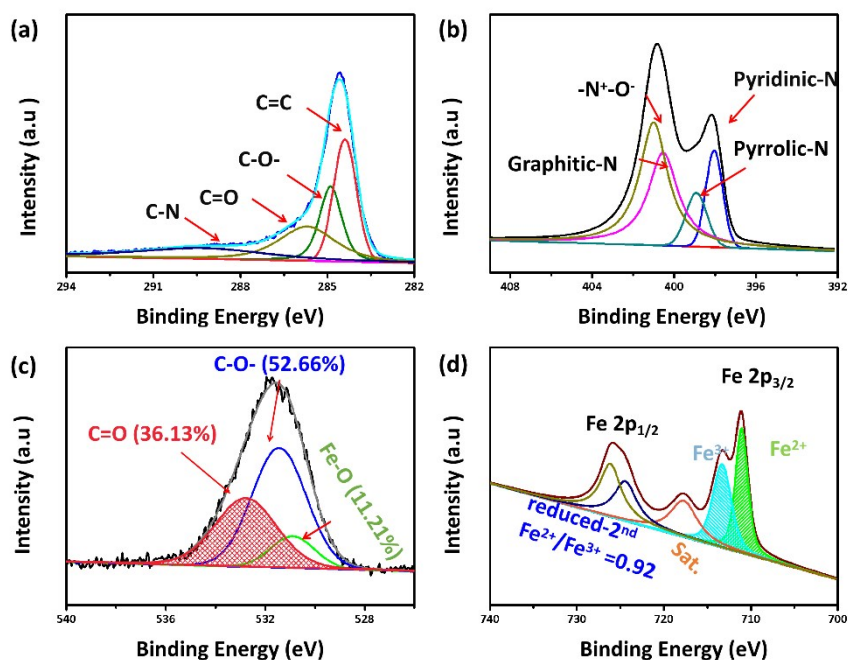


Figure S16. XPS narrowband distributed patterns of various temperature of reduced-2nd (a) C 1s; (b) N 1s; (c) O 1s; (d) Fe 2p.

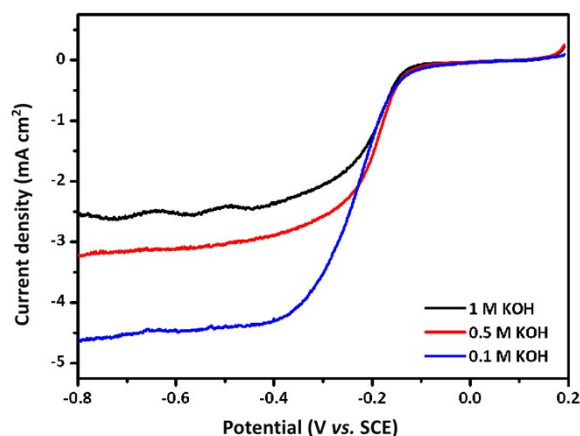


Figure S17. The LSV curves for Pt/C catalyst in various concentration of KOH under the rotate rate of 1600 rpm.

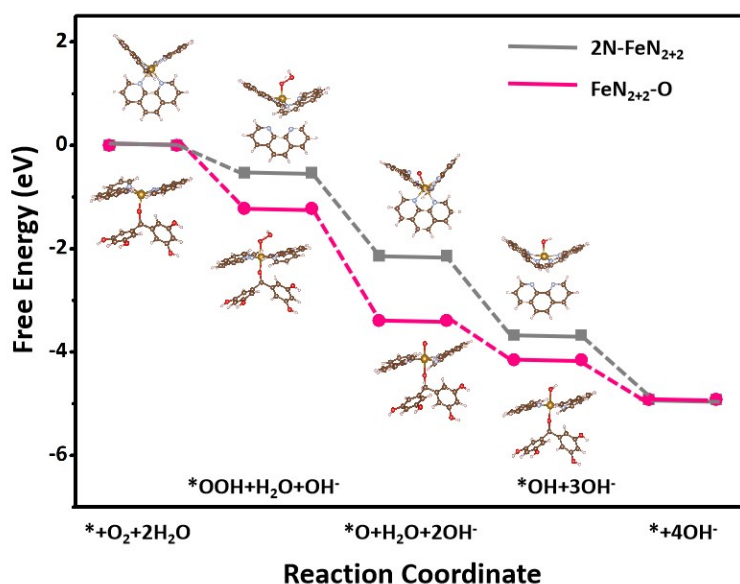


Figure S18. Free-energy diagram of the evolution of the FeN₄ and FeN₂₊₂O structure and under different oxygen reduction reaction pathway on the iron site. Inset shows the optimize structure of each pathway. The * denotes the adsorption on the material surface.

The ORR reaction process is accompanied by a dynamic cycling of hydrogenation and dehydrogenation of the intermediates, which are O₂ (ads), OOH (ads), O (ads), and OH (ads) in Figure S18. The O₂ molecule can readily be reduced to OH⁻ via a four-electron transfer pathway from both FeN₂₊₂-O and 2N-FeN₂₊₂ active sites. However, compared to 2N-FeN₂₊₂ (one Fe atom coordinated to six N atoms from three Phen), it can be observed that the FeN₂₊₂-O in which the Fe atom is coordinated to four N atoms from two Phen and one O atom from phenolic resin, can

reduce the reaction free energy of the $\cdot\text{OH}$, $\cdot\text{OO}$, $\cdot\text{O}$ and $\cdot\text{OOH}$ intermediates,^[12] which indicates the enhanced ORR performance.^[13] From the DFT calculation results, it can be found that the $\text{FeN}_{2+2}\text{-O}$ sites are similar to the D3 Fe-specie. Moreover, based on the variants reflecting from 2N- FeN_{2+2} in Figure 3, this model needs to break more frustration than $\text{FeN}_4\text{-O}$,^[14] so $\text{FeN}_4\text{-O}$ active sites can reduce much more free energy than 2N- FeN_{2+2} during ORR process. Therefore, the Fe-O bond should be also found to be significant in theory.

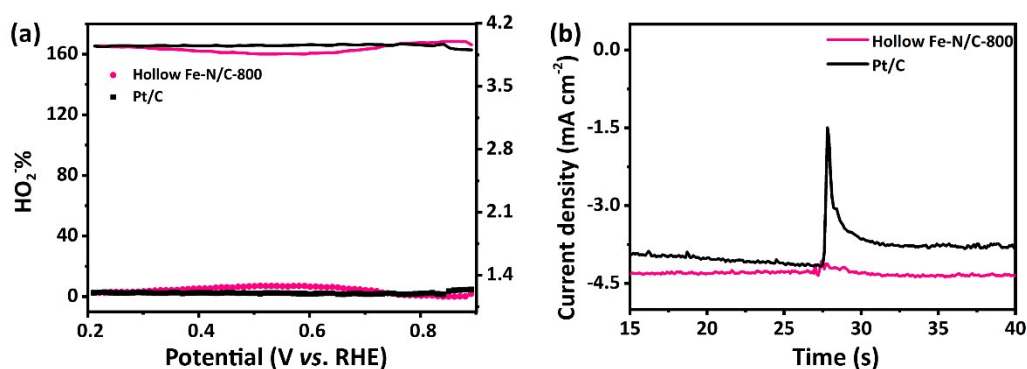


Figure S19. (a) The corresponding RRDE tests for Hollow Fe-N/C-800 and Pt/C; (b) the methanol tolerance test.

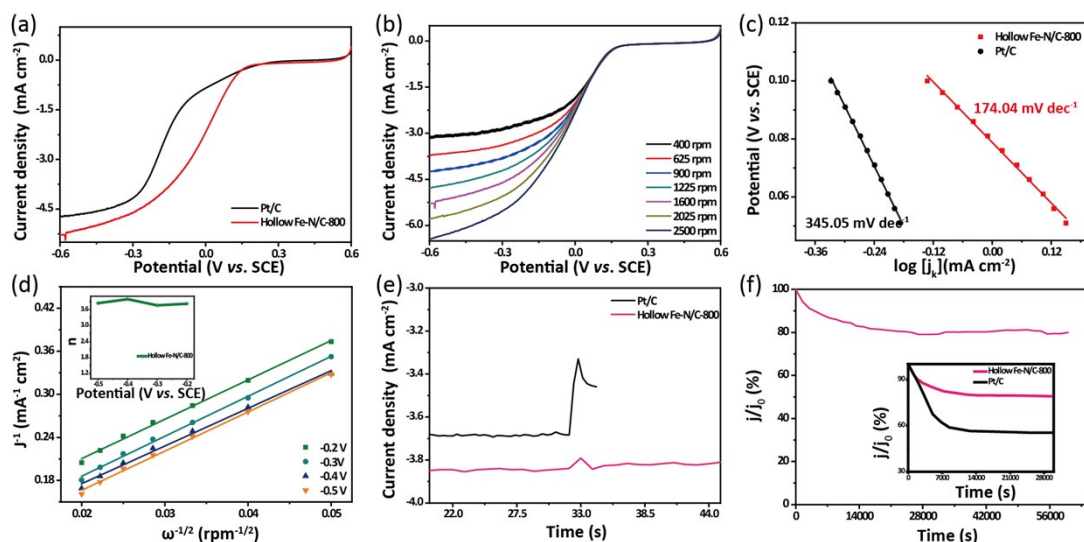


Figure S20. Corresponding electrochemical measurements. (a) LSV curves of Hollow Fe-N/C-800 and Pt/C; (b) LSV curves of Hollow Fe-N/C-800 at various rotation rates; (c) The corresponding K-L plots (j^{-1} vs. $\omega^{-1/2}$) at different potentials; (d) The electron-transfer number as function of potential; (e) chronoamperometric responses to the electrodes for injecting methanol into an O_2 saturated 0.1 M PBS solution at 0.2 V (vs. SCE); (f) chronoamperometric responses of those electrodes at 0.4 V (vs. SCE) in O_2 -saturated 0.1 M PBS solutions at a rotation rate of 1600 rpm, normalized to the initial current response.

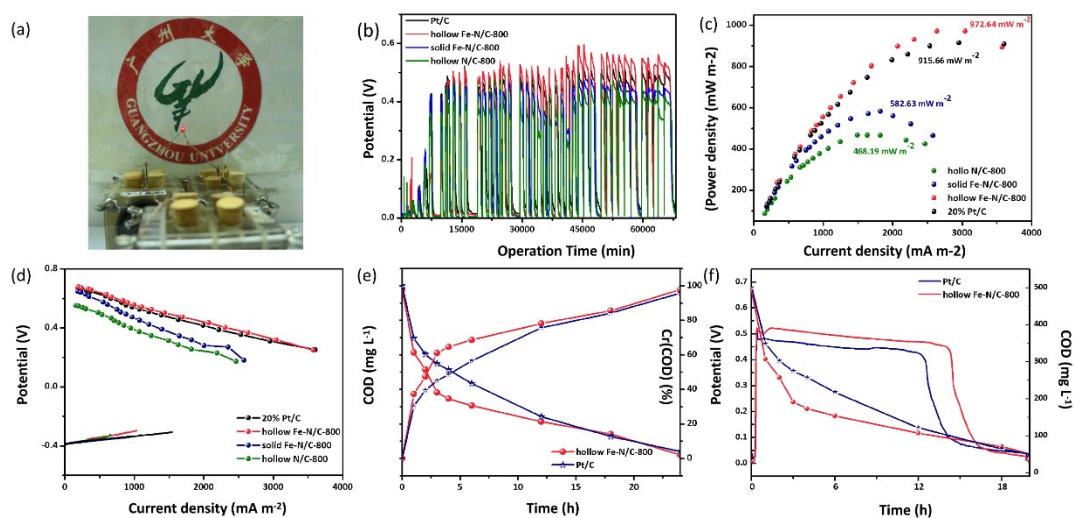


Figure S21. (a) Microbial fuel cell lighting diagram; (b) the V-t curves of samples for a MFCs device; (c) the power density of as-prepared and (d) their polarization curves of cathodes and anode; (e) the COD and removing rate curves of Hollow Fe-N/C and Pt/C; (f) the cyclic variation of CODs and v-t between Pt/C and Hollow Fe-N/C samples.

For Hollow Fe-N/C-800, only three 28 mL cells can light the red LED lamp for a long time (Figure S20a). From the v-t curves in Figure S20b, the voltage can be improved rapidly after replacing the culture solution. The average output voltage of MFC with Hollow Fe-N/C-800 (5.5 ± 0.3 V) is even higher than those with Pt/C (5.0 ± 0.2 V), solid Fe-N/C-800 (4.5 ± 0.3 V) and Hollow N/C-800 (4.0 ± 0.3 V). Analogously, the MFC equipped with Hollow Fe-N/C-800 catalyst exhibits the highest maximum power density (972.64 ± 0.4 mW cm⁻², Figure S20c), which is also even higher than that with Pt/C (915.66 ± 0.3 mW cm⁻²). Afterwards, the polarization curves of MFCs for anode and cathode are measured for maintain MFCs (Figure S20d). As we all known, MFCs has the double effects of simultaneously producing electricity and removing organic pollutant from wastewater. Hence the chemical oxygen consumption (COD) test of the MFCs is taken in this work. As shown in Figure S20 (e, f), the MFC with Hollow Fe-N/C-800 consume organic matter faster than that with Pt/C, indicating excellent potential in practical application.

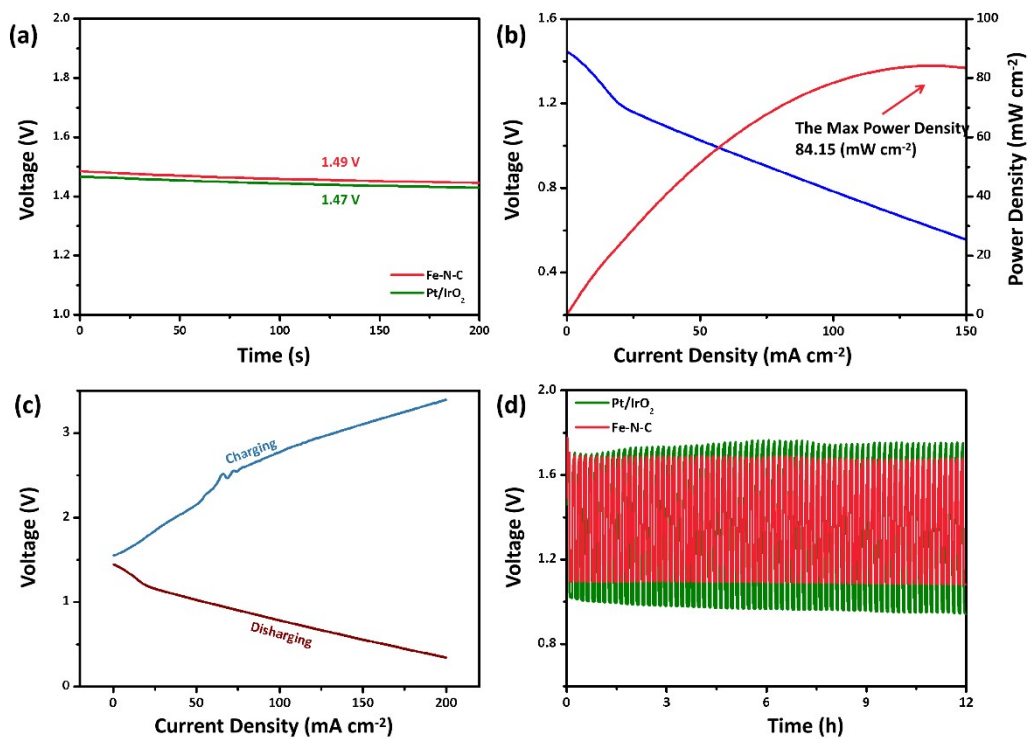


Figure S22. (a) Open circuit potential tests of Zn-air batteries coupling with Pt/IrO₂ or Fe-N-C as cathode; (b) the power density curves of Zn-air battery and (c) the charge-discharge test of Zn-air batteries for Fe-N-C; (d) cycle charge-discharge tests of Zn-air battery.

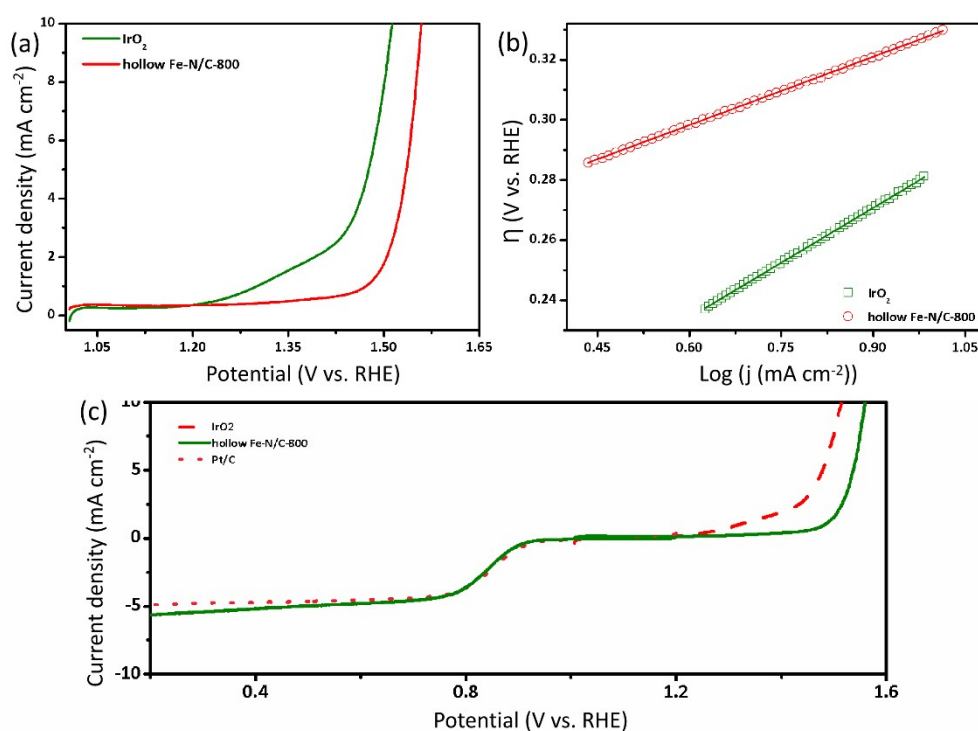


Figure S23. (a) LSV curves and Tafel plots (b) of Hollow Fe-N/C-800 and IrO₂ samples in 0.1 M KOH solution; (c) polarization curve measurement.

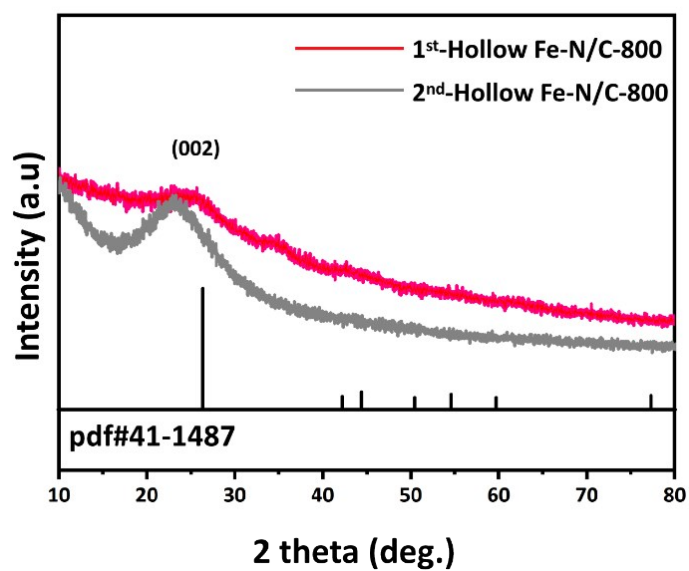


Figure S24. XRD pattern of 1st-Hollow Fe-N/C-800 and 2nd-Hollow Fe-N/C.

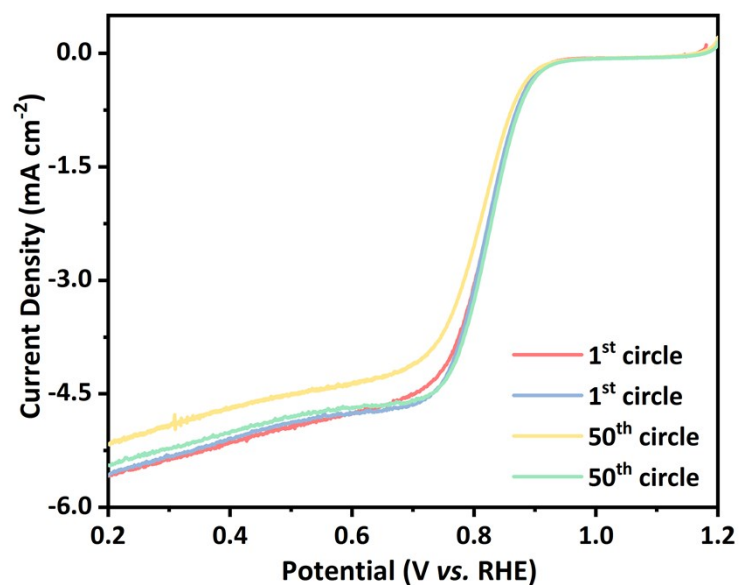


Figure S25. ORR polarization curves of Hollow Fe-N/C-800 obtained using a graphite or Pt counter electrode in O_2 -saturated 0.1 M KOH (red and yellow line were obtained with a graphite counter electrode, and blue and green line were obtained with a Pt counter electrode).

2. Supplementary Tables

Table S1 Elements contents of the catalysts in different temperatures from XPS survey spectrum.

Catalyst	C (at.%)	N (at.%)	O (at.%)	Fe (at.%)
Fe-N/C-700	83.23	3.13	13.36	0.28
Fe-N/C-800	86.39	2.69	10.65	0.28
Fe-N/C-900	90.06	1.61	8.09	0.26

Table S2 Elemental Compositions (O, N) Obtained by XPS Spectroscopy and Fe Contents Measured by ICP-AES

Catalyst	N (at.%)	O (at.%)	Fe (at.%)
Hollow Fe-N/C-800	2.69	10.65	6.38
Hollow N/C-800	3.87	8.03	S/A
Solid Fe-N/C-800	1.03	10.67	7.02

Table S3 Elemental Compositions (O, N) Obtained by XPS Spectroscopy and Fe Contents Measured by ICP-AES

Catalyst	N (at.%)	O (at.%)	Fe (at.%)
1 st -Hollow Fe-N/C-800	1.56	11.14	6.38
2 nd -Hollow Fe-N/C-800	1.47	9.14	6.02
Reduced-2 nd -Hollow Fe-N/C-800	1.53	14.29	5.40

Table S4 the deconvoluted C/N 1s peak positions under below sections from XPS data.

Element	Types	1 st -Hollow Fe-N/C-800	2 nd -Hollow Fe-N/C-800	Reduced-2 nd
C (at.%)	C=C	29.28	30.45	28.31
	C-O-	34.91	28.78	37.51
	C=O	18.21	23.43	16.41
	C-N	17.60	17.33	17.77
N (at.%)	Pyridinic-N	30.51	25.96	29.12
	Pyrrolic-N	22.41	21.82	20.35
	graphite-N	28.01	30.12	29.21
	N-oxide	19.06	22.10	21.32