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Supporting Information

Phenolic/resin assisted MOFs derived hierarchical Co/N-doping carbon rhombic dodecahedron for electrocatalysis

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Materials and Methods:

Materials:

2-methylimidazole (2-MeIm), $Co(NO_3)_3 \cdot 6H_2O$, 4-aminophenol, formaldehyde (37%), potassium hydroxide (KOH) and nafion were purchased from Sigma-Aldrich. Anhydrous ethanol and sulfuric acid (H_2SO_4) were obtained from Nanjing Chemical Reagent Co., Ltd. All the reagents were directly used without further purification. Deionized (DI) water was used all the experiments.

Synthesis of ZIF-67 nanoparticles. In a typical experiment, 20.0 g of 2-MeIm was added to 300 mL of DI water with stirring for 10 min. Then 1.2 g of $Co(NO_3)_2 \cdot 6H_2O$ dissolved in 150 mL solution (DI water/ethanol = 2/1) was added into the above solution with stirring for 12 h at room temperature. The resultant purple precipitate was collected by centrifugation with 8000 r/min for 10 min and washed with DI water and ethanol for three times, respectively. Finally, the purple powder was dried under vacuum 6 h at 80 ˚C.

Synthesis of AF nanoparticles. 20.0 g of 2-MeIm and 1.0 mL of formaldehyde were added to 300 mL of DI water with stirring for 15 min. 0.5 g of 4-aminophenol dissolved in 150 mL solution (DI water/ethanol = 2/1) was added into the above solution with stirring for 12 h at room temperature. The resultant black precipitate was collected by centrifugation with 8000 r/min for 10 min. After drying, condensation AF was obtained.

Synthesis of *x*-ZIF-67@AF/ nanoparticles. In a typical synthesis. 20.0 g of 2-MeIm and 1.0 mL of formaldehyde were added to 300 mL of DI water with stirring for 15 min. Then 1.2 g of $Co(NO_3)_2 \cdot 6H_2O$ and 0.45 g of 4-aminophenol dissolved in 150 mL solution (DI water/ethanol = 2/1) was added into the above solution with stirring for 12 h at room temperature. The resultant brown precipitate was collected by centrifugation with 2000 r/min for 5 min and washed with DI water and ethanol for three times, respectively. After drying, composite ZIF-67@AF was obtained. The composites 0.5-ZIF-67@AF and 1.5-ZIF-67@AF were obtained used the same method except 4-aminophenol was 0.23 and 0.68 g, respectively.

Synthesis of 1.0-HZPC-7/8/9, x-HZPC-8, ZIF-67-8 and AF-8 nanoparticles. HZPC-7/8/9 were prepared from directly carbonized ZIF-67@AF in N_2 atmosphere at different temperature 700, 800 and 900 ˚C, respectively. *x*-HZPC-8, ZIF-67-8 and AF-8 were obtained by carbonizing the corresponding precursor in N_2 atmosphere at 800 ˚C.

Characterization: The structure and morphology of samples were confirmed by TEM (FEI T20), STEM (Tecnai G2 F30 S-TWIN), SEM (FEI 250 and JEOL 7800). The composition was investigated by XRD

(BRUKER D8, Cu Kα) at 40 kV and 40 mA (λ = 1.5418Å). The N_2 adsorption and desorption isotherms were obtained from Micromeritics ASAP-2020 instrument. X-ray photoelectron spectroscopy (XPS) spectra were obtained by using a PHI Quantera II ESCA System with Al Kα radiation at 1486.8V. Raman spectroscopy was conducted at Renishaw in Via reflex spectrometer system.

Electrochemical Measurement. The electrochemical measurement of HZPC-7/8/9, *x*-HZPC-8, ZIF-67-8 and AF-8 and Pt/C for ORR were carried out in a three-electrode cell (CHI 760E, CH Instrument, Shanghai). The Ag/AgCl electrode (3 M KCl), platinum sheet and sample-modified glassy carbon were the reference, counter electrode and working electrode, respectively. The working electrode was prepared according to previous literature. 10 mg of catalyst was dispersed in 2 mL of mixed solution of ethanol/water (70/30) and ultrasonic dispersion for 15 min. Then the rotary disk electrode (diameter 5 mm) was covered over with 75 μL of catalyst dispersion. After drying, 7.5 μL of nafion solution (10% in ethanol) as the binder was dripped on the surface of catalyst. Finally, the prepared electrode was dried at 50˚C for 3 h. Cyclic voltammetry (CV) tests were measured from 0.1 to 1.1 V versus reversible hydrogen electrode (RHE) in N_2/O_2-saturated 0.1 M KOH (0.5 M H_2SO_4) aqueous solution (the scan rate: 10 mV s^{-1}). Linear sweep voltammogram (LSV) tests were carried out under different rotations in a N_2/O_2-saturated 0.1 M KOH (0.5 M H_2SO_4) electrolyte (scan rate: 10 mV s^{-1}). Current–time (*I–t*) tests were performed at the rotation rate of 1600 rpm in a 0.1 M KOH aqueous solution. electrochemical impedance spectroscopy (EIS) were measured in the frequency range of 0.01−100 000 Hz with 5 mV alternating current amplitude.

The electron transfer numbers (*n*) were obtained according to the Koutecky–Levich (*K–L*) equation, as follows:

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

$$n = \frac{B}{0.2F(D_0)^{2/3}(V)^{-1/6}C_0} \quad (2)$$

$$j_k = nFkC_0 \quad (3)$$

where j and j_k correspond to measured and kinetic-limited current densities, respectively; B can be determined from the slope of the K-L plots; ω is the rotation rate (rpm); F is the Faraday constant (96485 C mol^{-1}); D_0 is the diffusion coefficient of oxygen (1.9×10^{-5} cm^2 s^{-1}, 0.1 M KOH); V is the kinematic viscosity of the electrolyte (0.01 cm s^{-1}, 0.1 M KOH); C_o is the concentration of oxygen (1.22×10^{-6} mol cm^{-3}).

The rotating ring-disk electrode (RRDE) cures at 1600 rpm with a scan rate of 10 mV s^{-1}, and the

hydrogen peroxide yield (%H_2O_2) is calculated by the following equation:

$$\%H_2O_2 = 200\frac{I_{r/}N}{I_d + I_{r/}N}$$

where I_d and I_r are the disk and ring current, respectively. N is the ring current collection efficiency which is determined to be about 0.35 in a 10 mM $K_3[Fe(CN)_6]$ and 0.1 M KNO_3 solution.

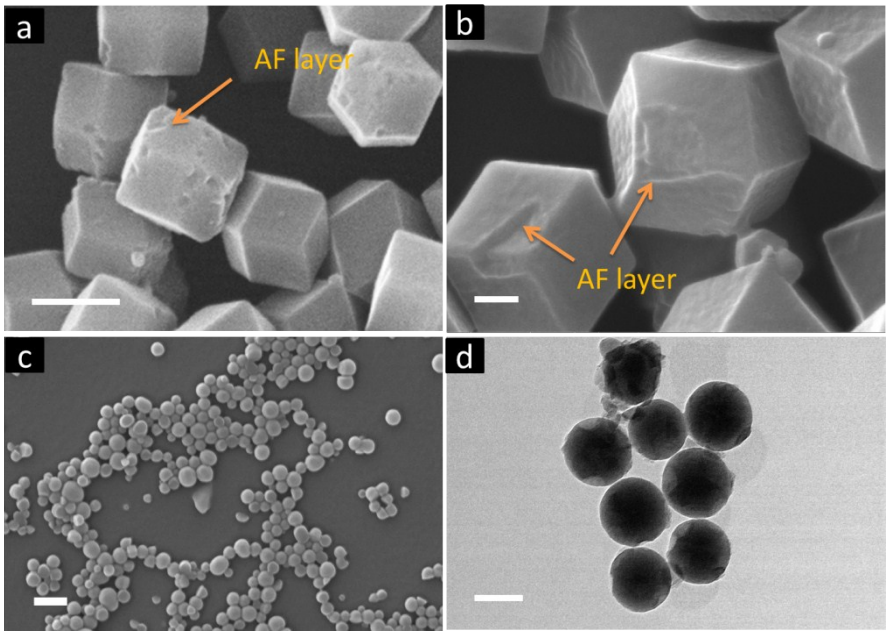

Fig. S1 (a) and (b) the enlarge SEM images of 0.5-ZIF-67@AF and 1.5-ZIF-67@AF, respectively; (c) and (d) the SEM and TEM images of AF, respectively. The scale bar is 200 nm for (a), (b) and (d); 500 nm for (c).

Fig. S2 the digital pictures of ZIF-67, 0.5-ZIF-67@AF, 1.0-ZIF-67@AF and 1.5-ZIF-67@AF from left to right.

Table S1 Textural parameters and proportion of carbon, nitrogen, oxygen calculated by XPS of the samples.

Samples	S_{BET} ($m^2\ g^{-1}$)	V_{Pore} ($cm^3\ g^{-1}$)	Elementary composition (%)		
			N	C	O
1.0-HZPC-7	439.3	0.26	5.6	82.1	12.3
1.0-HZPC-8	509.9	0.42	4.8	86.7	8.5
1.0-HZPC-9	297.9	0.33	1.6	90.8	7.6
ZIF-67-8	303.6	0.18	3.7	83.5	12.8
0.5-HZPC-8	354.8	0.22	/	/	/
1.5-HZPC-8	483.8	0.36	/	/	/
AF-8	328.2	0.21	/	/	/

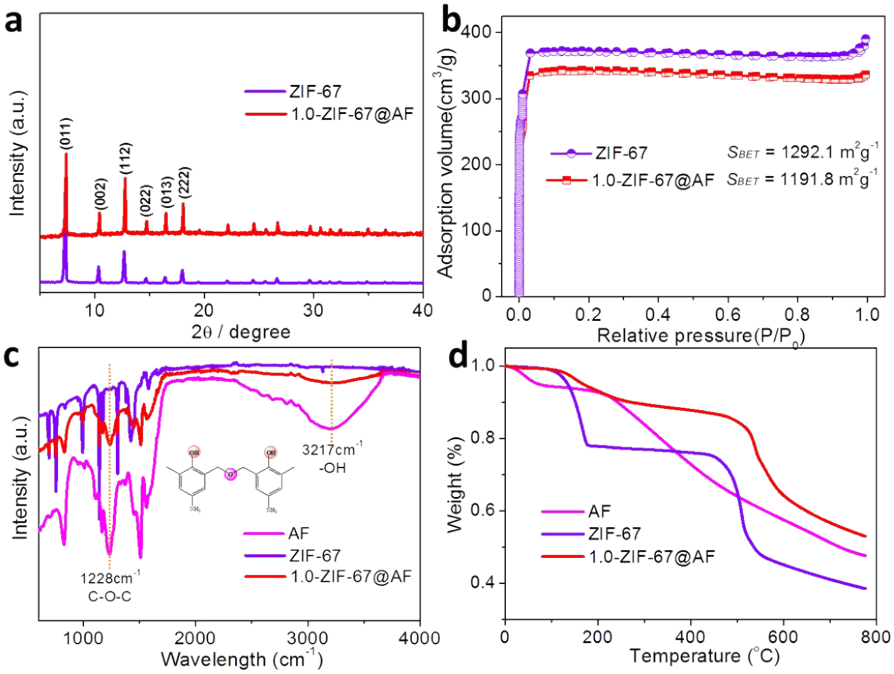

Fig. S3 (a) the XRD patterns of as-synthese ZIF-67 and 1.0-ZIF-67@AF; (b) N_2 adsorption and desorption isotherms of ZIF-67 and 1.0-ZIF-67@AF; (c) the IR spectra of AF, ZIF-67 and 1.0-ZIF-67@AF; (d) thermogravimetry analysis curves of AF, ZIF-67 and 1.0-ZIF-67@AF under the heating rate of 5 ˚C min^{-1} in N_2 atmosphere.

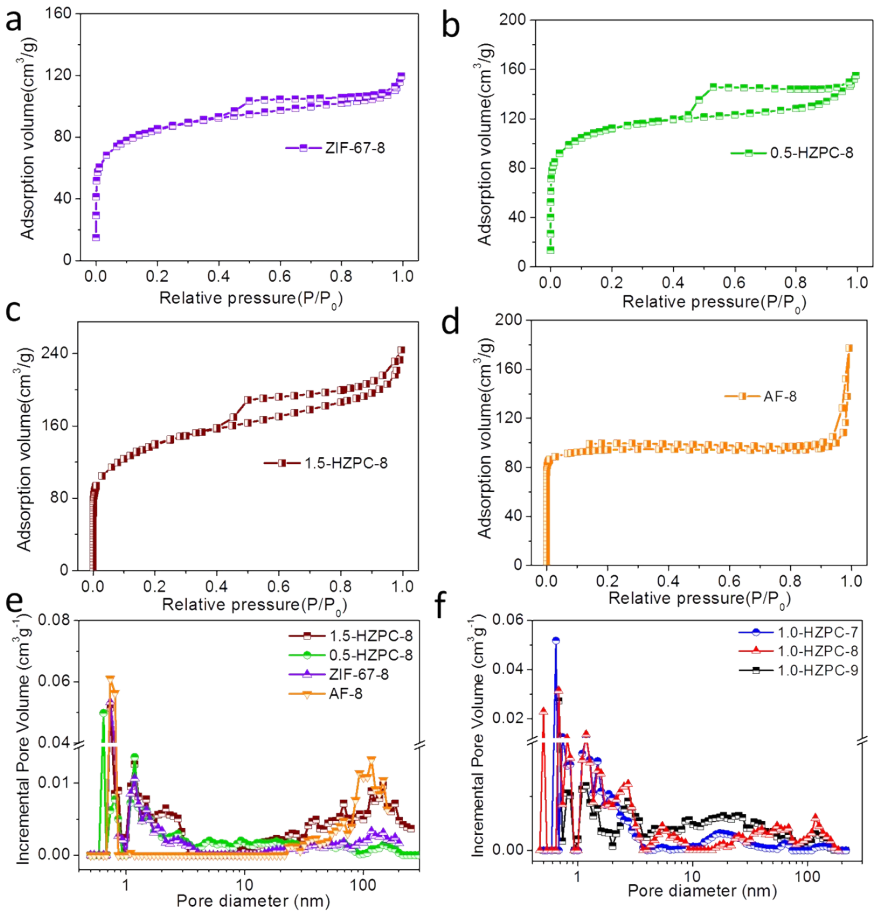

Fig. S4 (a-d) N_2 sorption/desorption isotherms of ZIF-67-8, 0.5-HZPC-8, 1.5-HZPC-8 and AF-8; (e, f) the pore size distribution of ZIF-67-8, 0.5/1.5-HZPC-8, AF-8 and 1.0-HZPC-7/8/9.

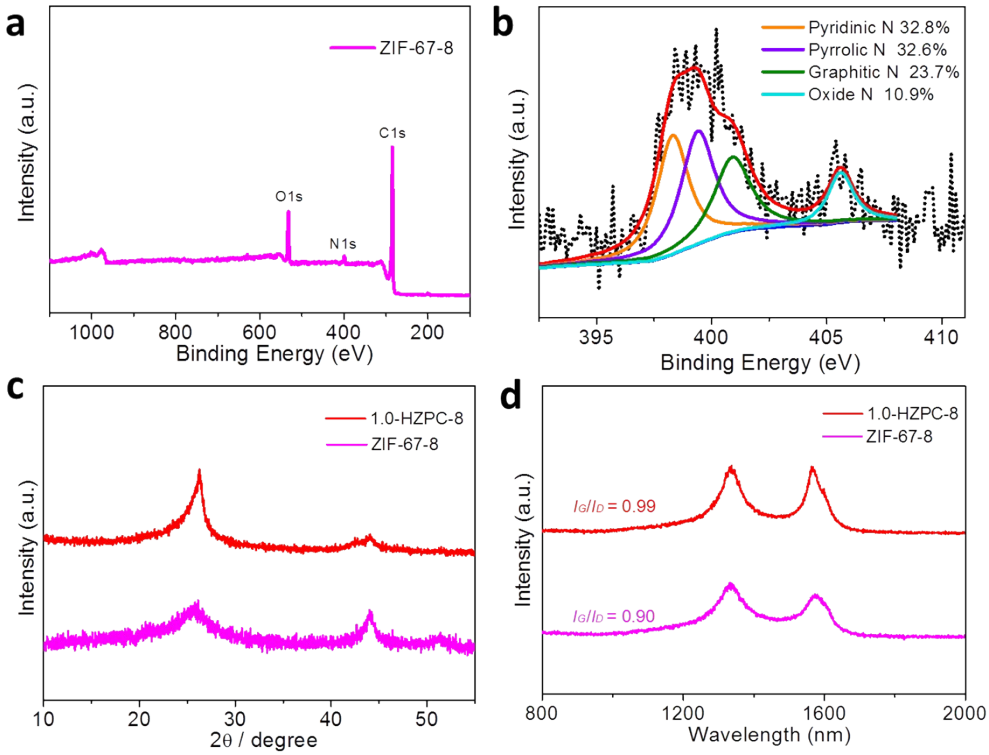

Fig. S5 (a) and (b) the wide-range XPS and high resolution N1s spectra of ZIF-67-8 obtained at 800˚C; (c) and (d) the XRD and Raman spectra of 1.0-HZPC-8 and ZIF-67-8, respectively.

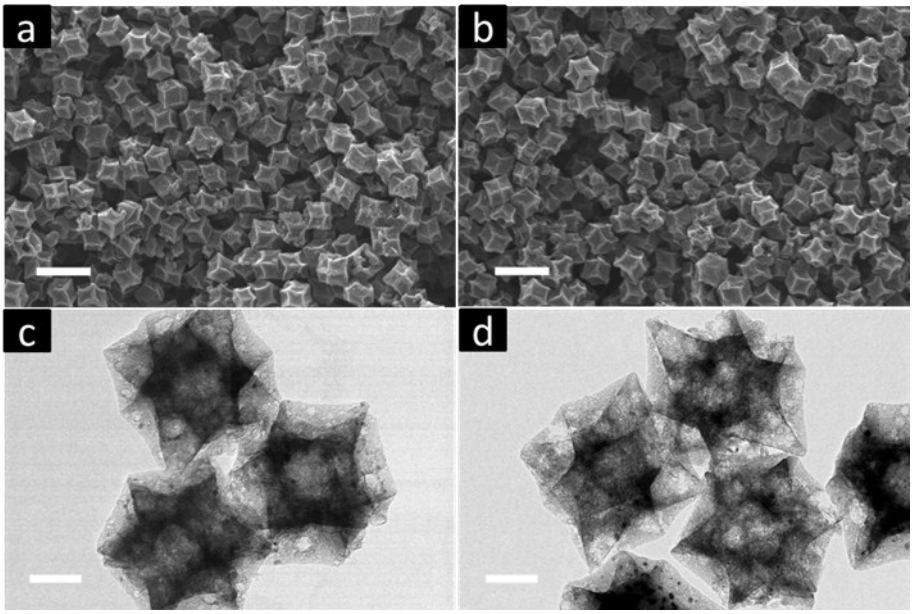

Fig. S6 (a) and (b) the SEM images for 1.0-HZPC-7 and 1.0-HZPC-9, respectively, the scale bar is 1 μm; (c) and (d) The TEM images for HZPC-7 and HZPC-9, respectively, the scale bar is 200 nm.

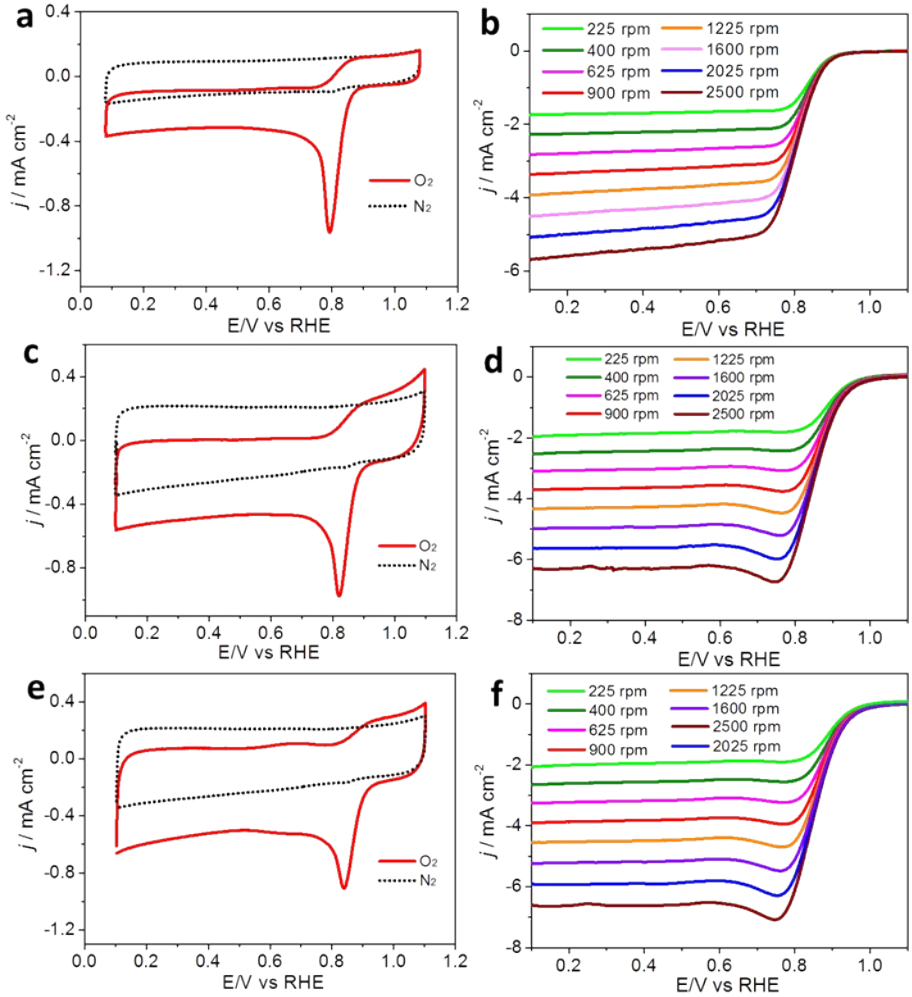

Fig. S7 (a-e) CVs and LSV curves of ZIF-67-8, 0.5-HZPC-8 and 1.5-HZPC-8 at a scan rate of 10 mV/s in N_2/O_2-saturated 0.1 M KOH solution, respectively.

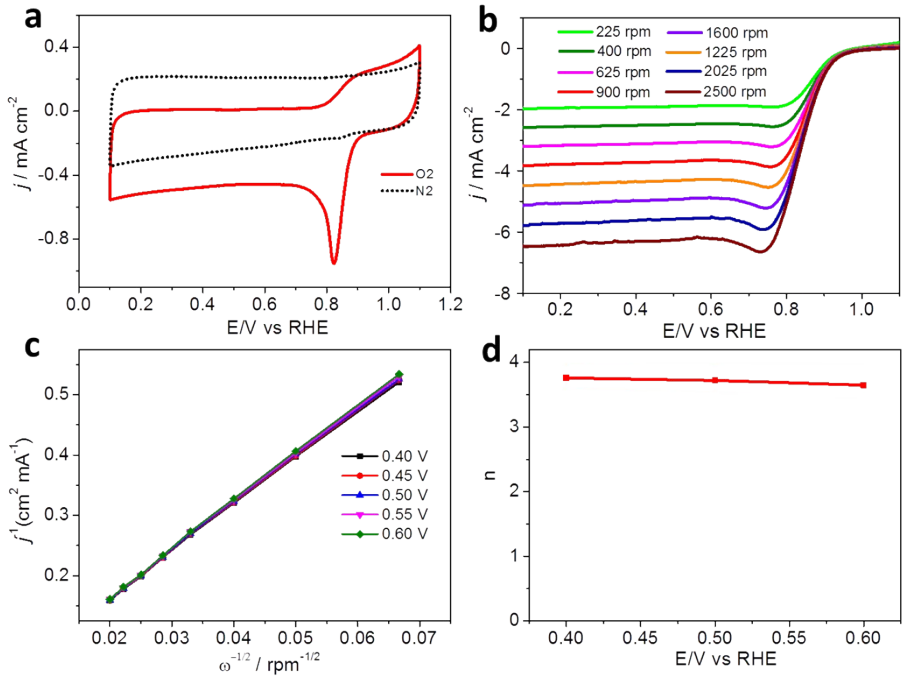

Fig. S8 (a) CVs of 1.0-HZPC-7 at a scan rate of 10 mV/s in N_2/O_2-saturated 0.1 M KOH solution; (b) different rotation speeds of polarization curves, (c) K-L plots, and (d) electron transfer numbers of 1.0-HZPC-7 in O_2-saturated 0.1 M KOH solution.

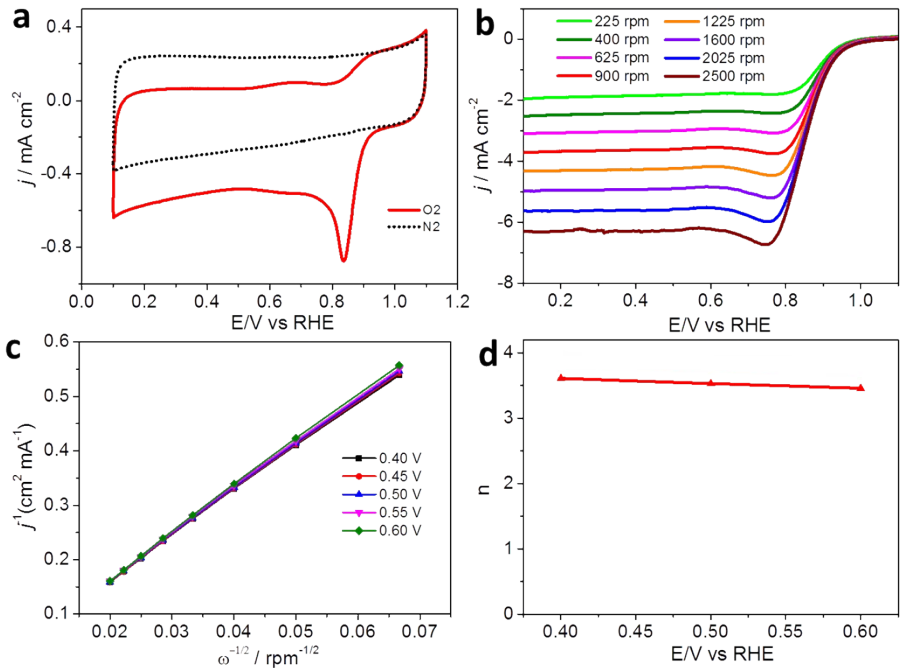

Fig.S9 (a) CVs of 1.0-HZPC-9 at a scan rate of 10 mV/s in N_2/O_2-saturated 0.1 M KOH solution; (b) different rotation speeds of polarization curves, (c) K-L plots, and (d) electron transfer numbers of 1.0-HZPC-9 in O_2-saturated 0.1 M KOH solution.

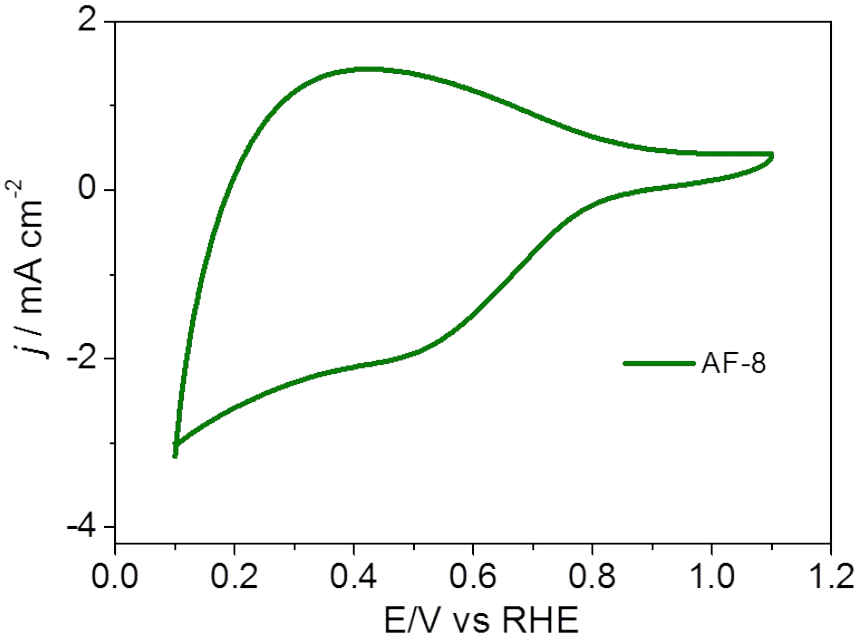

Fig. S10 CV curve of AF-8 at a scan rate of 10 mV/s in O_2-saturated 0.1 M KOH solution.

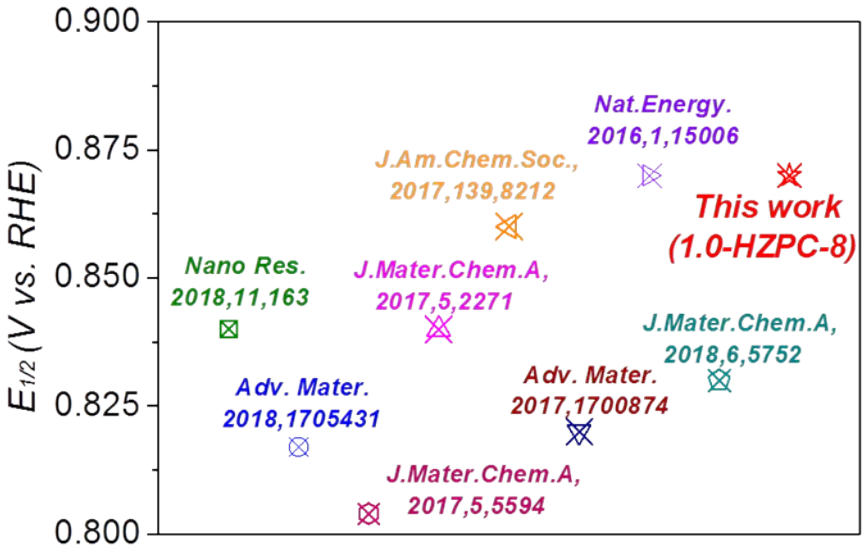

Fig. S11 the comparative of ORR performance of Co/N-doped carbon materials.

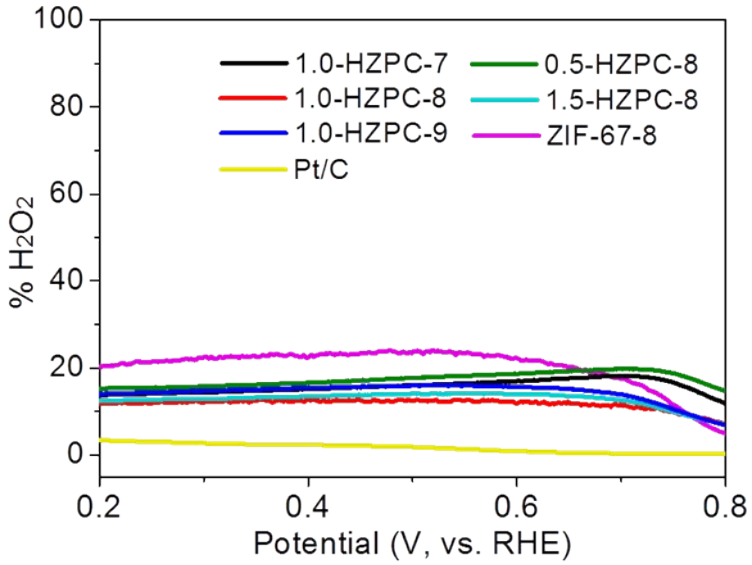

Fig. S12 H_2O_2 yield of Pt/C, 1.0-HZPC-7/8/9, 0.5/1.5-HZPC-8 and ZIF-67-8 at various potentials based on RRDE data.

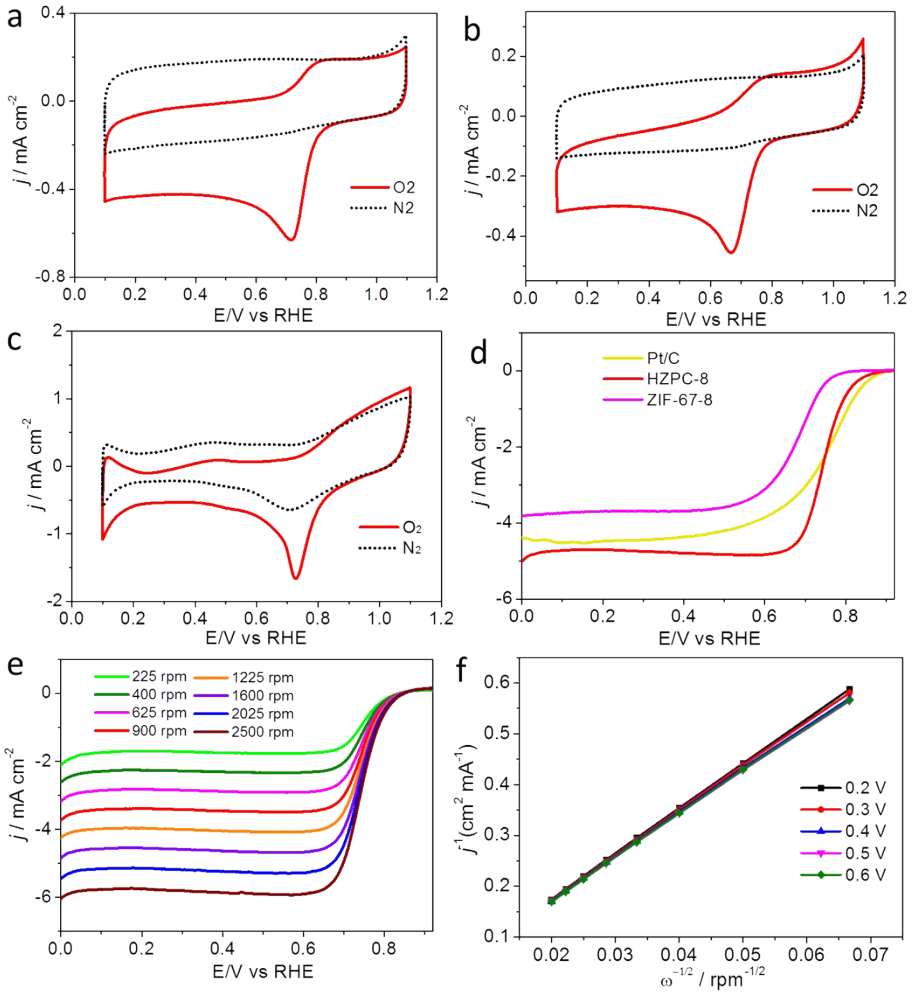

Fig. S13 CVs curves of (a) 1.0-HZPC-8, (b) ZIF-67-8 and (c) Pt/C at a scan rate of 10 mV/s in N_2/O_2-saturated 0.5 M H_2SO_4 solution; (d) LSV curves of 1.0-HZPC-8, ZIF-67-8 and Pt/C in O_2-saturated 0.5 M H_2SO_4 solution; (b) different rotation speeds of polarization curves and (c) K-L plots of 1.0-HZPC-8 in O_2-saturated 0.5 M H_2SO_4 solution.

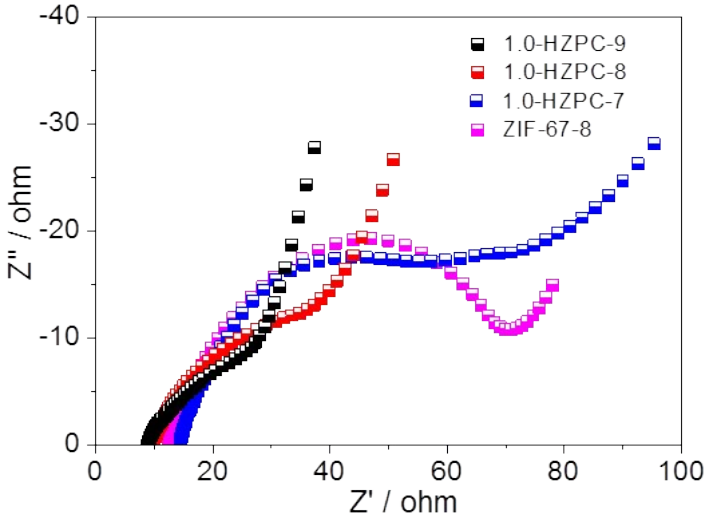

Fig. S14 Nyquist plots of ZIF-67-8 and 1.0-HZPC-7/8/9 in the frequency range of 0.01-100000 Hz.

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