

Supporting Information

Zeolitic-imidazolate Framework (ZIF)@ZnCo-ZIF Core-shell Template-derived Co, N-doped Carbon Catalysts for Oxygen Reduction Reaction

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1. Experimental Section

1.1 Materials

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 2-methylimidazole (2-mIM) were analytical grade and bought from Shanghai Macklin Biochemical Co., Ltd, China. Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were purchased from Acros Organics company. Anhydrous methanol and ethanol was bought from Beijing Chemical Works (Beijing, China). Potassium hydroxide (KOH) was bought from Sinopharm Chemical Reagent Co., Ltd. Commercial Pt/C catalyst (20 wt% Platinum on Vulcan XC-72) was received from Premetek Co. Ltd. Nafion solution (5 wt%) was obtained from DuPont Company. All raw chemicals were used without further purification.

1.2 Synthesis of catalysts

1.2.1 Synthesis of core-shell op-ZnCo-ZIF. Core-shell op-ZnCo-ZIF was synthesized by a facile one-pot method under room temperature based on a previous method.^{S1} $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (729 mg) and 2-methylimidazole (526 mg) were dissolved in methanol (40 mL) respectively to form to clear solutions. Then they were mixed together and stirred for 2.5 hours. Without separation the white ZIF-8 seed crystals, another pink clear methanolic solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (79.2 mg, 3 mL) and a methanolic solution of 2-mIM (526 mg, 3 mL) were stepwise (10 min interval) injected into the above mixture. After stirring for another 2.5h, the violet products (named as op-ZnCo-ZIF) were separated by filter, washed by methanol for several times and dried in an oven under 60 °C for one night.

1.2.2 Synthesis of ZIF-67. ZIF-67 was prepared similarly. A methanolic solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.164 g, 40 mL) and a methanolic solution of 2-mIM (2.63g, 40 mL) were mixed together and stirred for 5 h. Then, similarly, the purple products (ZIF-67) were separated by filter, washed by methanol for several times and dried in an oven under 60 °C for one night.

1.2.3 Synthesis of op-ZnCo-ZIF-950 and ZIF-67-950. First, 0.4 g op-ZnCo-ZIF precursor was placed into a ceramic boat. Then, we put it into a tube furnace. In order to remove air, a constant Ar stream was kept at rate of 80 mL min⁻¹ in the tube furnace

for 5 h. Subsequently, the sample was heated to 950 °C at a rate of 3 °C min⁻¹ and kept for 2 h. Finally, it cooled down to room temperature. Ar atmosphere was kept during the whole pyrolysis procedure at a rate of 80 mL min⁻¹. The resulting sample was labeled as op-ZnCo-950. Similarly, ZIF-67-950 was obtained by carbonizing the ZIF-67 sample as the former pyrolysis procedure.

1.3 Physicochemical Characterizations

Scanning electron microscope (SEM) images were captured by HITACHI S-4800. High-resolution transmission electron microscope (HRTEM) images, high-angle annular dark field-scanning transmission electron microscope (HAADF-STEM) images, elemental mappings and line scan images were obtained using a FEI Tecnai F20 field emission transmission electron microscope, operating at 200 kV. Powder X-ray diffraction (PXRD) was carried out using a D8 ADVANCE X-ray diffractometer with Cu K α radiation (40 kV, 20 mA, $\lambda = 1.54178 \text{ \AA}$). Raman spectra were obtained through a LabRAM Aramis Raman Spectrometer. N₂ adsorption/desorption analysis was performed by an ASAP 2460 analyzer (Micromeritics, U.S.A) at 77 K. The outgas procedure for all samples was conducted under 200 °C and hold for at least 6 h under vacuum. X-ray photoelectron spectroscopy (XPS) measurements were carried out by a Thermo Fisher ESCALAB 250 X-ray photoelectron spectrometer equipped with a twin anode Mg-K α X-ray source. The X-ray Absorption Fine Structure (XAFS) spectra was collected at the beamline 4W1B of Beijing Synchrotron Radiation Facility (BSRF). The storage rings of BSRF were operated at 2.5 GeV with a maximum current of 250 mA. The EXAFS data were collected using a fixed-exit double-crystal Si (111) monochromator. Co K-edge EXAFS data were analyzed using standard procedures with the IFEFFIT software packages.

1.4 Electrochemical measurements

A CHI 760e electrochemical workstation (Shanghai Chenhua Instrument Factory, China) was used to carry out all electrochemical measurements, connecting with a rotator (RRDE-3A, ALS Co., Ltd, Japan). All electrochemical measurements were performed with a three-electrode system at room temperature in 0.1 M KOH aqueous

solution (pH = 13). A saturated calomel electrode (SCE) served as the reference electrode. Potentials in this paper normalized to a reversible hydrogen electrode (RHE) was converted according to the Nernst equation ($E_{\text{RHE}} = E_{\text{SCE}} + 0.245 \text{ V} + 0.059\text{pH}$).^{S2} A polished Pt wire was used as the counter electrode. A rotating ring-disk electrode (RRDE, 4.0 mm in diameter) were served as the substrate for the working electrodes.

For the fabrication of the working electrode, 5 mg of each sample (including 20 wt% Pt/C catalyst) was dispersed by 0.25 mL ethanol and 0.75 mL DI water, with 50 μL Nafion solution (5 wt %). The mixture solution was ultrasonicated for at least 30 min to obtain the homogeneous dispersion. Then, 6.4 μL of the dispersion was dropped onto the RRDE electrode disk with loading of $\sim 0.25 \text{ mg cm}^{-2}$, followed by drying under room temperature. The RRDE measurement was carried out with the Pt ring electrode potential of -0.4 V (*vs* SCE). The catalytic route of the catalyst can be evaluated according the H_2O_2 yield and the electron transfer number (n). The H_2O_2 yield and electron transfer number (n) can be calculated by using the following equations:

$$n = 4 \times \frac{I_{\text{disk}}}{(I_{\text{ring}}/N) + I_{\text{disk}}} \quad (\text{Eq. S1})$$

$$\text{H}_2\text{O}_2 (\%) = 200 \times \frac{I_{\text{ring}}/N}{(I_{\text{ring}}/N) + I_{\text{disk}}} \quad (\text{Eq. S2})$$

where I_{disk} is the disk current, measured by the glassy carbon electrode, and I_{ring} is the ring current, measured with a Pt ring electrode. N is the ring collection efficiency (0.37).^{S3}

The kinetics parameters of ORR can be analyzed using the Koutecky-Levich (K-L) equation^{S4, 5} shown as follows:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \quad (\text{Eq. S3})$$

$$B=0.62nFD_0^{2/3}\nu^{-1/6}C_0 \quad (\text{Eq. S4})$$

where j is the measured current density, j_k is the kinetic current density, ω is the rotation rate of the disk electrode, n is the number of electron transfers per O_2 molecule, F is the Faraday constant (96485 C mol^{-1}), C_0 is the bulk oxygen concentration in 0.1 M KOH ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$), D_0 is the oxygen diffusion

coefficient in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and ν is the kinematic viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$).^{S5}

2. Supplementary Figures

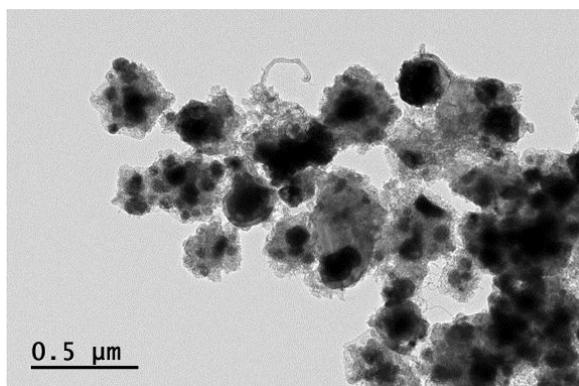


Figure S1. TEM image of ZIF-67-950.

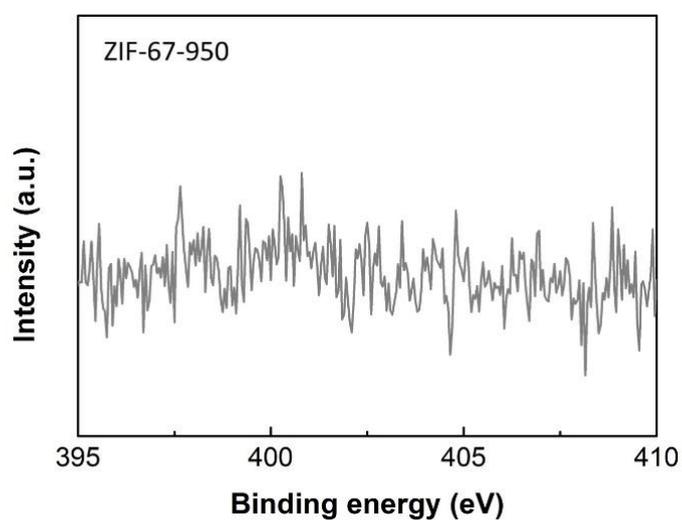


Figure S2. XPS spectra of N in ZIF-67-950.

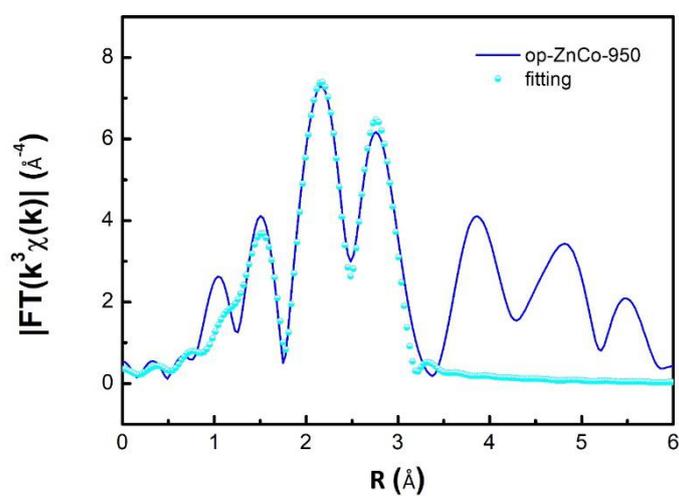


Figure S3. Fourier-transformed Co K-edge spectra of op-ZnCo-950 and fitting curve.

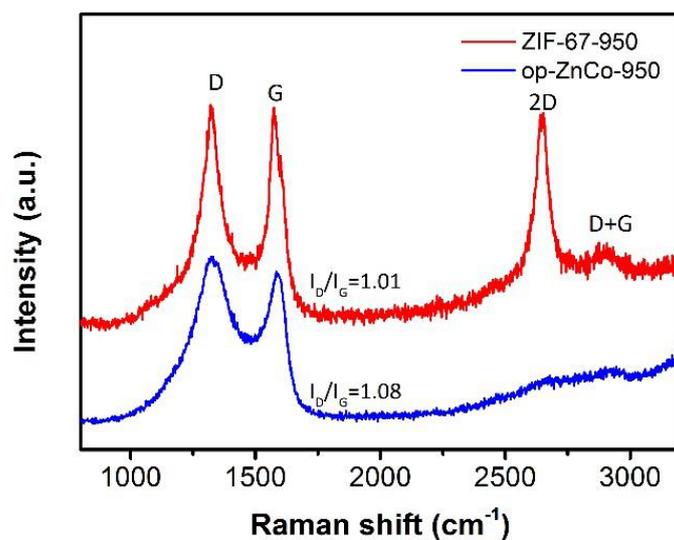


Figure S4. Raman spectra of op-ZnCo-950 and ZIF-67-950.

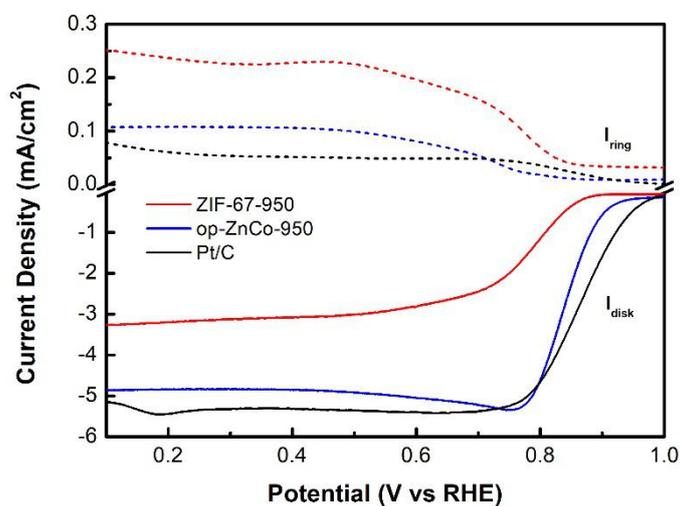


Figure S5. RRDE polarization curves of ZIF-67-950, op-ZnCo-950 and commercial 20 wt% Pt/C, in 0.1 M KOH, under oxygen bubbling at scan rate of 10 mV s^{-1} and electrode-rotation speed of 1600 rpm. (Solid line for disk current density and dash line for ring current density.)

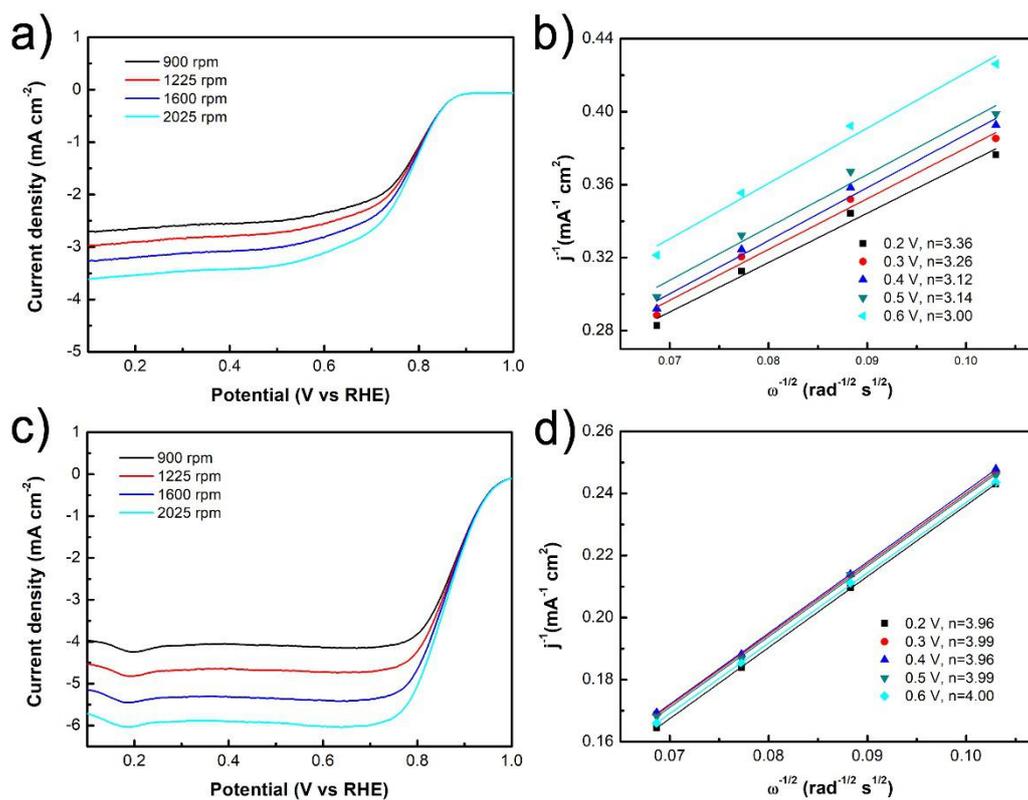


Figure S6. The LSV curves, corresponding Koutecky-Levich plots and the electron transfer numbers (inset) at different potentials of ZIF-67-950 (a, b) and 20 wt% Pt/C (c, d). LSV curves were recorded in O₂-saturated 0.1 M KOH solution under different rotational speeds with a sweep rate of 10 mV s⁻¹.

3. Supplementary Tables

Table S1. BET specific surface areas of op-ZnCo-ZIF, ZIF-67, op-ZnCo-950 and ZIF-67-950.

	Sample	BET SSA (m ² /g)
ZIFs precursor	op-ZnCo-ZIF	1483
	ZIF-67	1584
ZIFs derived carbon	op-ZnCo-950	1144
	ZIF-67-950	133.6

Table S2. Elemental content results (atomic content, %) of op-ZnCo-950 and ZIF-67-950 from XPS.

Sample	C	N	Co	O
op-ZnCo-950	89.03	4.23	0.66	6.08
ZIF-67-950	80.93	1.15	0.78	17.15

Table S3. XPS typical N peak fitting results (atomic content, %) of op-ZnCo-950.

Pyridinic N	Co-N	Pyrrolic N	Graphitic N	Oxidized N	Total N
1.29	0.69	0.47	1.10	0.68	4.23

Table S4. EXAFS fitting parameters at the Co K-edge for op-ZnCo-950.

Path	N^a	R (Å) ^b	σ^2 (Å ² ·10 ³) ^c	ΔE_0 (eV) ^d	R factor (%)
Co-N(O)	2.5	1.90	6.9	-8	
Co-Co	1.5	2.50	3.5	-4.3	1.4
Co-O-Co	4.4	3.06	8.5	9.7	

^a N : coordination numbers; ^b R : bond distance; ^c σ^2 : Debye-Waller factors; ^d ΔE_0 : the inner potential correction. R factor: goodness of fit. S_0^2 , 0.80, was obtained from the experimental EXAFS fit of CoO reference by fixing CN as the known crystallographic value and was fixed to all the samples.

4. References

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