

Supporting Information

Controllable Synthesis of CoN₃ Catalysts Derived from Co/Zn-ZIF-67 for Electrocatalytic Oxygen Reduction in Acidic Electrolytes

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Experimental materials and methods

Materials: Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), methanol, ethanol were purchased from Sinopharm Chemical Reagent (Shanghai, China) and used without further purification. The organic ligand, 2-methylimidazole, was purchased from J&K Chemistry Company (Shanghai, China). Nafion perfluorinated resin solution containing 5% Nafion was purchased from Sigma-Aldrich.

Synthesis of n-ZIF-67: The synthesis of ZIF-67 particles was according to the previous reported method with some modification. Typically, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.6011 g, 2.06 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (8.1190 g, 27.29 mmol) were dissolved in a mixed solution of 100 mL methanol and 100 mL ethanol. The 2-methylimidazole ligand (9.8523 g, 119.97 mmol) was dissolved in a mixed solution of 100 mL methanol and 100 mL ethanol, and then this solution was added to the former salt solution under continue stirring for 15 s. The final solution was kept at room temperature for 20 h. The purple precipitation (7-ZIF-67) was collected by filtration and washed with methanol three times and dried at 60 °C overnight. Other ZIF-67 precursors with a range of Co contents were synthesized by a similar procedure, except for the metal contents. To facilitate, the ZIF-67 precursors were designated as n-ZIF-67, where the n (n = 3, 5, 7, 9, 10) is expressed as the molar percentage of Co again total metals (Co and Zn) in the starting materials.

Synthesis of $\text{CoN}_3@NC-n-T$: The Co/Zn-ZIF-67 precursors were subsequently heated at a temperature ranging from 900 to 1100 °C for 2 h with the heating rate of 5 °C min^{-1} under Ar atmosphere and cooled down to room temperature naturally. The obtained N-doped nanocarbon-based CoN_3 catalysts were labeled as $\text{CoN}_3@NC-n-T$, where n is the molar percentage of Co again total metals (Co and Zn) in the starting materials and T is the carbonization temperature.

Synthesis of the contrast sample: In order to prove that the ZIF-67 as the precursor is necessary to obtain CoN_3 compound, we mixed the compounds of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.6011 g, 2.06 mmol), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (8.1190 g, 27.29 mmol) and 2-methylimidazole ligand (9.8523 g, 119.97 mmol) evenly. Then the mixture was heated at 1000 °C for 2 h with the heating rate of 5 °C min^{-1} under Ar

atmosphere and cooled down to room temperature naturally. Finally, the dark green powder was obtained.

Characterization: The phase structures were characterized by powder X-ray diffraction (XRD, DX2700, China) at the rate (2θ) of 2° min^{-1} ranging from 5° to 90° , using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) with the accelerating voltage of 40 kV and the applied current of 30 mA. The morphology and structure of the samples were investigated by the field emission scanning electron microscopy (FESEM) (JSM-7001F, JEOL, Tokyo, Japan). Transmission electron microscope (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-TEM) images were obtained using a JEM-2100F with an accelerating voltage of 200 kV. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET, JW-BK132F, Beijing) method from data in a relative pressure (P/P_0) range from 0.05 and 0.20. Pore size distribution plots were derived from the adsorption branch of the isotherms. Raman spectroscopy were recorded on a Renishaw 1000 Raman spectrometer with the 514.5 nm excitation line of an Ar ion laser. The chemistry composition was analyzed by X-ray photoelectron spectroscopy (XPS) using an ESCALab250 electron spectroscopy (Thermo Scientific Corporation) with monochromatic 150 W Al K α radiation.

Electrochemical measurements: The electrochemical studies were performed in a standard three-electrode configuration by a CHI 760E electrochemistry workstation. Glassy carbon electrode, Ag/AgCl and graphite rod were used at working electrode, reference electrode and counter electrode, respectively. An ink of the catalyst solution was prepared by 4 mg of catalyst powder in the mixture solution of 50 μL of a 5 wt% Nafion solution, 250 μL ethanol and 250 μL deionized water, and then further placed in an ultrasonic bath. Afterwards, 10 μL of the electrocatalyst ink was pipetted onto the surface of the pre-cleaned rotating disk electrode (RDE) (4 mm diameter, loading $\sim 0.58 \text{ mg cm}^{-2}$) and dried at room temperature to yield a thin-film electrode before measurement. A 20 wt % Pt/C with a loading mass of about 0.12 mg cm^{-2} was used for reference.

In ORR experiment, 0.5 M H_2SO_4 solution was universally used as the electrolyte. Cyclic voltammetry (CV) with a scan rate of 50 mV s^{-1} was obtained in the potential range of 1 to -0.4 V vs.

Ag/AgCl at the room temperature under O₂- or N₂ flow. Linear sweep voltammetry (LSV) was recorded in O₂- or N₂-saturated 0.5 M H₂SO₄. The potential range of the LSV measurements is -0.2 ~ 1.0 V (vs. Ag/AgCl). ORR polarization curves were performed in O₂-saturated electrolyte at a scan rate of 10 mV s⁻¹ under various electrode rotation rates (400, 625, 900, 1225, 1600, 2025, 2500 rpm). All the measured potentials in this work were converted to a reversible hydrogen electrode potential (E_{RHE}) with Nernst equation (E_{RHE} = E_{AgCl} + 0.059 pH + 0.197).

The rotating ring-disk electrode (RRDE) test in acidic media was conducted using a graphite rod as counter electrode and the Ag/AgCl as reference electrode. The RRDE measurements were carried out with the rotating rate of 1600 rpm and the ring potential was set at 1 V with a scan rate of 10 mV s⁻¹. The electron number (*n*) and the peroxide ions (H₂O₂ %) were determined by the following equation:

$$n = \frac{4NI_D}{NI_D + I_R} \dots\dots\dots\text{(I)}$$

$$H_2O_2(\%) = \frac{200I_R}{NI_D + I_R} \dots\dots\dots\text{(II)}$$

where I_D is disk current, I_R is ring current, and N = 0.43 is the current collection efficiency of the Pt ring. The loading amount of CoN₃@NC-7-1000 for RRDE measurements is ~ 0.58 mg cm⁻².

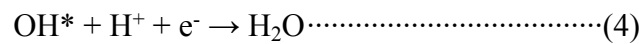
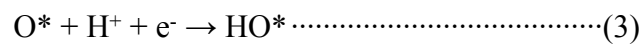
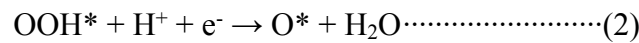
The stability of the catalyst was tested by using the corresponding current-time (*i-t*) chronoamperometric response in O₂-saturated 0.5 M H₂SO₄ solution at a rotating rate of 1600 rpm and a potential of 0.1 V. The methanol tolerance of the catalyst was tested by recording the chronoamperometric response in O₂-saturated 0.5 M H₂SO₄ at 0.4 V with a rotation rate of 1600 rpm. 3 M methanol was rapidly injected into 0.5 M H₂SO₄ solution with in ≈ 500 s after starting the chronoamperometric measurement.

Electrochemical measurements for single cell: A single cell fixture (Pragma Industries, France) was used and the flow field was single serpentine for both cathode and anode. The geometric area of the cell is 5 cm². The channel/land ratio for the flow fields is 3:2, the depth of the channels is 1.2 mm. The cell fixture was applied 2 N mm⁻² pressure by a cell compression unit (Pragma Industries, France)

during the whole test. Nitrogen was fed into anode and cathode during heating up process. For the whole experimental, ca. 0.2 L min⁻¹ air (or O₂) and ca. 0.1 L min⁻¹ hydrogen were fed into cathode and anode separately, under ambient pressure. The temperature of the cell compression unit was controlled at 70 °C. The catalyst loading of CoN₃@NC-7-1000 on the cathode side was 4.0 mg cm⁻².

The performance and stability tests were measured by a Fuel Cell Testing System (Arbin Instruments, USA). For steady-state operation, the single cell was operated under a constant load of 200 mA cm⁻². For dynamic-state operation, the cell was subjected to potential cycles between the open circuit voltage (OCV) for 3 min and 0.5 V for 30 s. The basis for choosing these loading profiles for degradation analysis was to mimic a practical fuel cell system operating at the normal condition (working voltage of 0.6-0.7 V), or under heavy duty (i.e. high current) and shutdown circumstances.

DFT calculations: The overall ORR in an acid environment can be written as follows:



Where * donates the active sites on the catalyst. The Gibbs free energy ΔG of each step is obtained by the following equation:

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S + \Delta G_{\text{U}} + \Delta G_{\text{pH}} \dots\dots\dots(\text{III})$$

Where ΔE , ΔZPE , and ΔS represent the different intermediate energy, zero-point energy changes, and entropy of the reaction, respectively. ΔE was obtained from DFT calculations, and ΔZPE and ΔS were calculated from the values in Jia et al.¹ Each step of ΔG was obtained as follows:

$$\Delta G_1 = \Delta G_{\text{OOH}} - eU + \Delta G_{\text{H}^+} - 4.92\text{eV} \dots\dots\dots(\text{IV})$$

$$\Delta G_2 = \Delta G_{\text{O}} - \Delta G_{\text{OOH}} - eU + \Delta G_{\text{H}^+} \dots\dots\dots(\text{V})$$

$$\Delta G_3 = \Delta G_{\text{OH}} - \Delta G_{\text{O}} - eU + \Delta G_{\text{H}^+} \dots\dots\dots(\text{VI})$$

$$\Delta G_4 = \Delta G_{\text{OH}} - eU + \Delta G_{\text{H}^+} \dots\dots\dots(\text{VII})$$

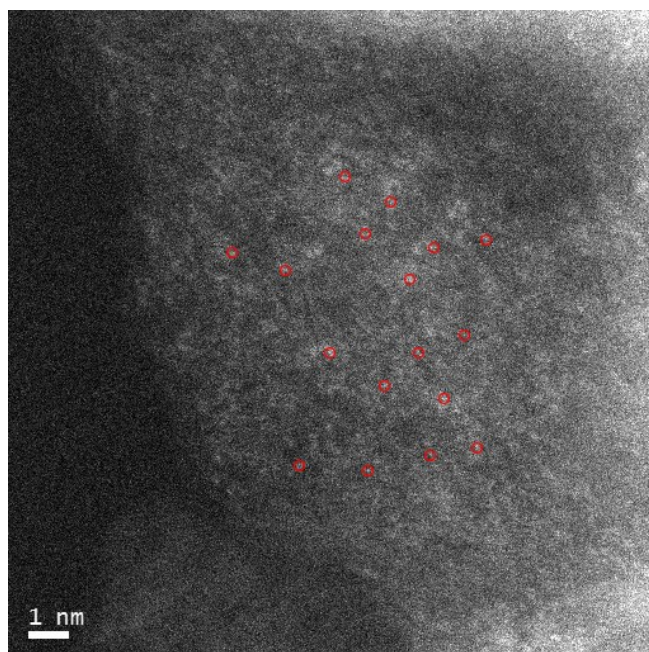


Fig. S1 Aberration-corrected HAADF-STEM image of Co@NC-3-1000 (the bright dots marked by red circles are single-atom Co).

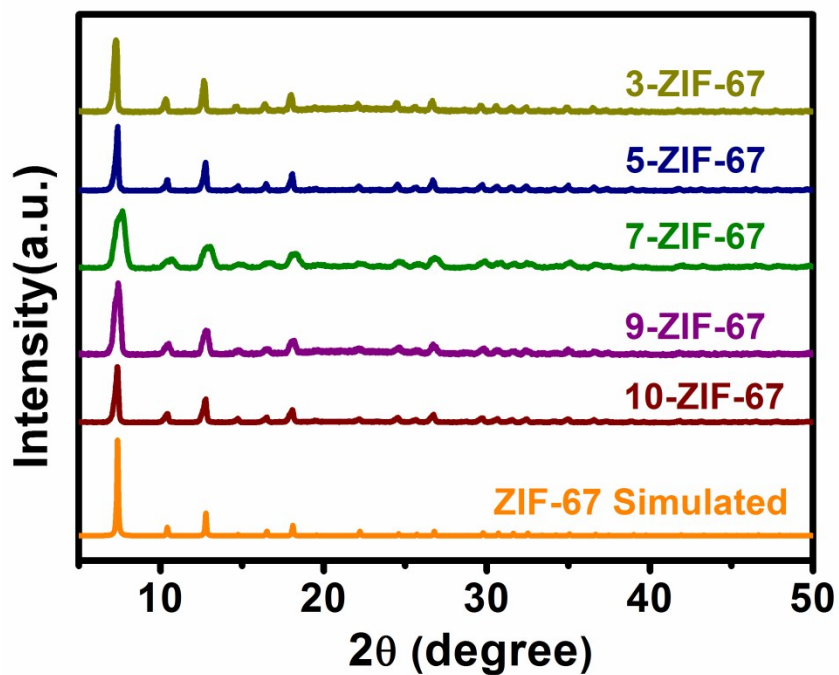


Fig. S2 XRD pattern of 3-ZIF-67, 5-ZIF-67, 7-ZIF-67, 9-ZIF-67, 10-ZIF-67 and ZIF-67 simulated.

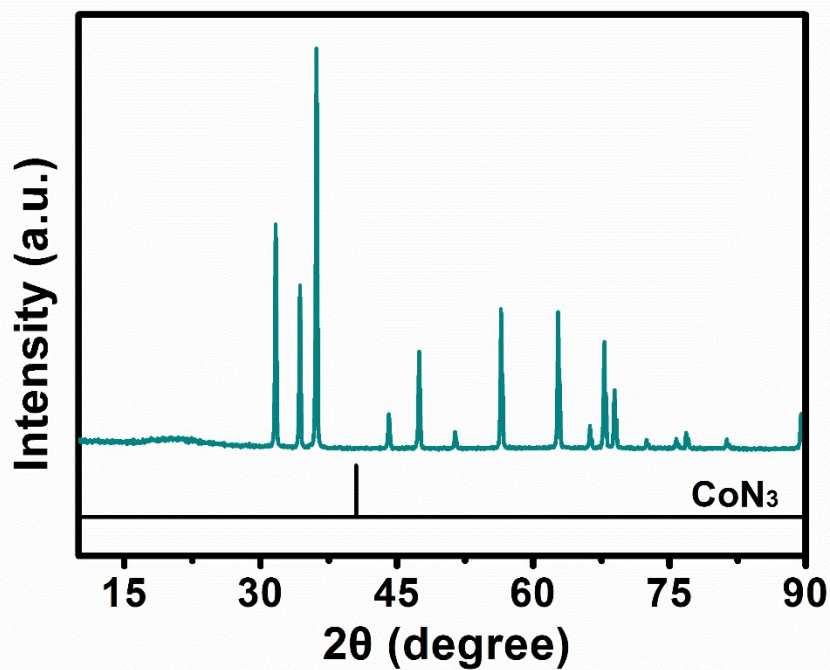


Fig. S3 XRD pattern of the contrast sample.

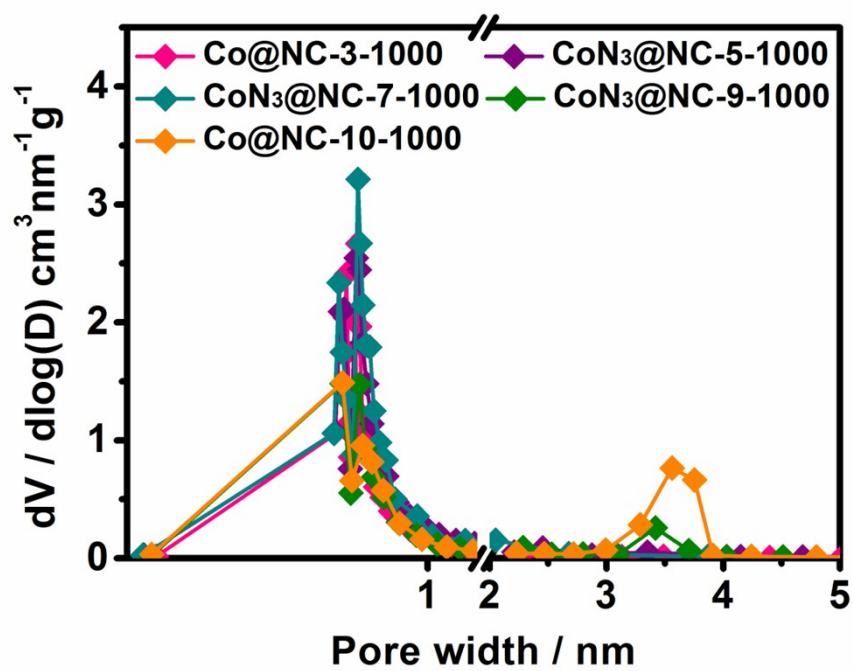


Fig. S4 Pore size distributions of Co@NC-3-1000, CoN₃@NC-5-1000, CoN₃@NC-7-1000, CoN₃@NC-9-1000 and Co@NC-10-1000.

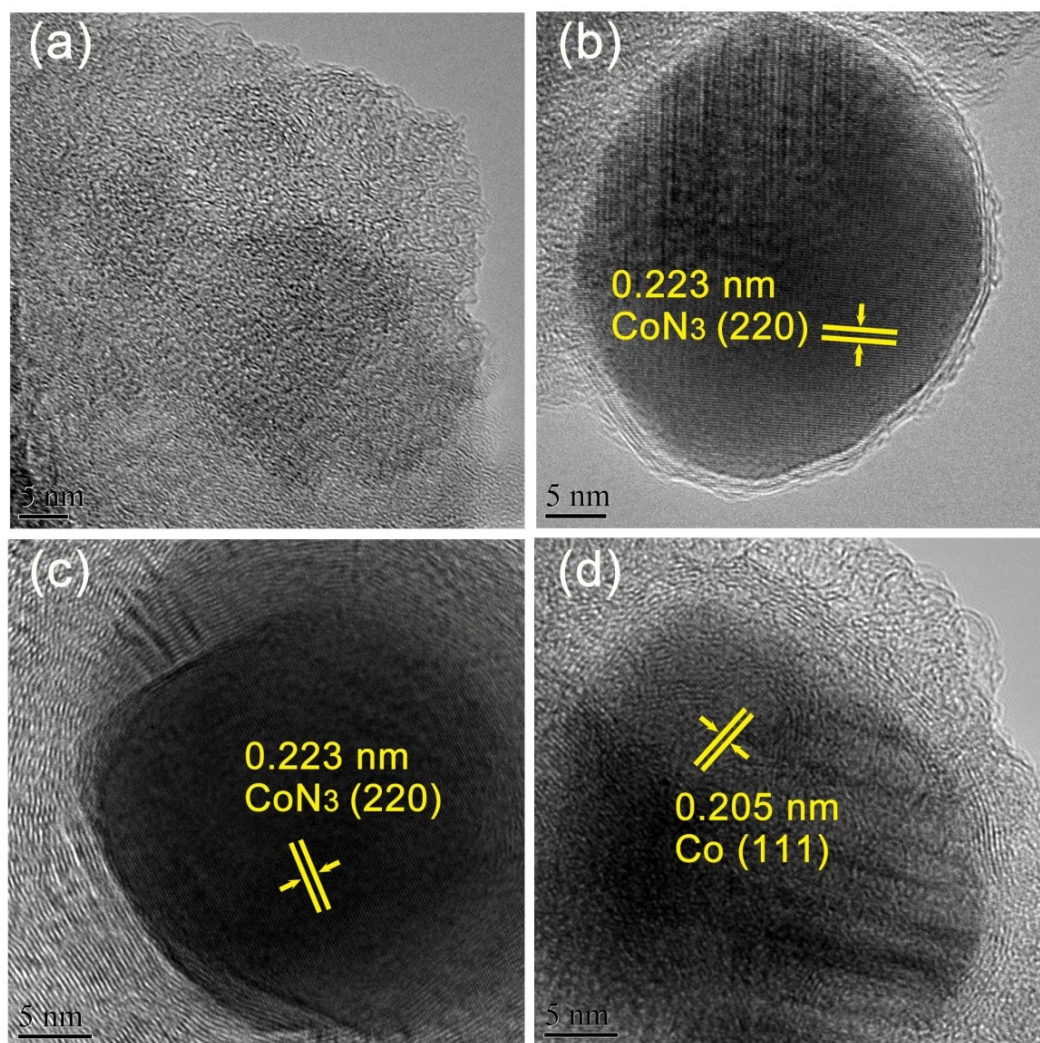


Fig. S5 HRTEM of (a) Co@NC-3-1000, (b) CoN₃@NC-5-1000, (c) CoN₃@NC-9-1000 and (d) Co@NC-10-1000.

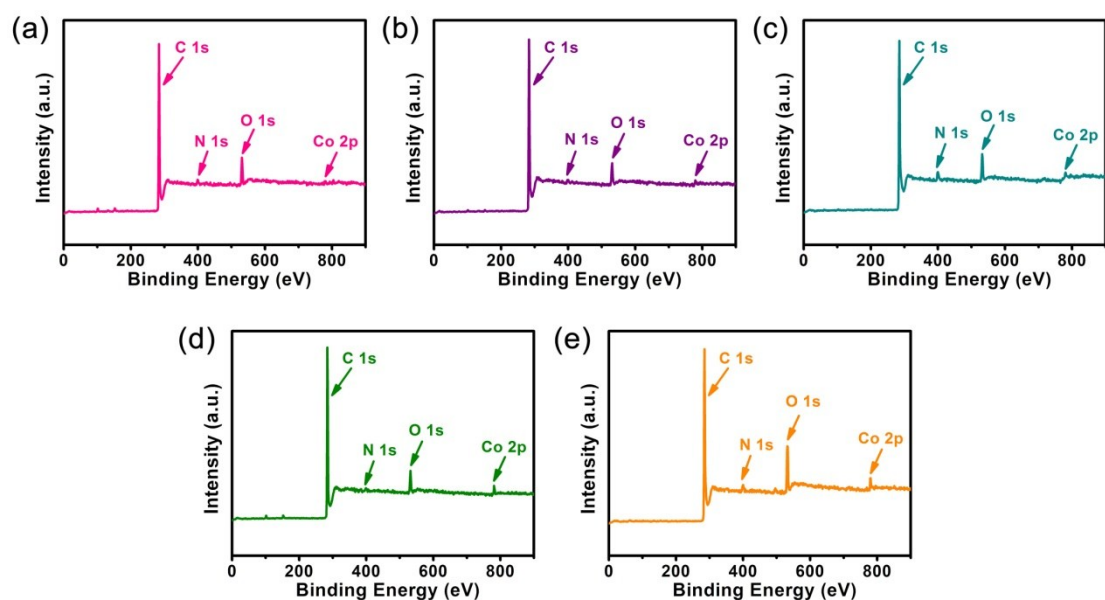


Fig. S6 XPS survey scan spectra (a) Co@NC-3-1000. (b) CoN₃@NC-5-1000. (c) CoN₃@NC-7-1000. (d) CoN₃@NC-9-1000 and (e) Co@NC-10-1000.

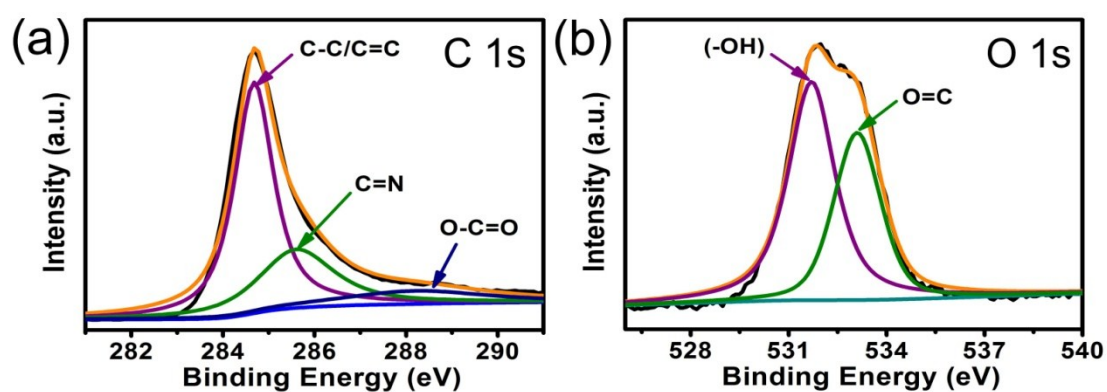


Fig. S7 XPS spectra of CoN₃@NC-7-1000: (a) C 1s, and (b) O 1s.

Table S1. ORR Electrocatalytic Performance of the Samples.

Sample	medium	E_0 (V) ^{a)}	$E_{1/2}$ (V) ^{b)}	J (mA cm ⁻²) ^{c)}
Co@NC-5-900	0.5 M H ₂ SO ₄	0.76	0.66	-4.86
CoN ₃ @NC-5-1000	0.5 M H ₂ SO ₄	0.78	0.72	-4.52
CoN ₃ @NC-5-1100	0.5 M H ₂ SO ₄	0.72	0.62	-4.08

^{a)} E_0 , onset potential, acquired at an ORR current density of -0.1 mA cm^{-2} ; ^{b)} $E_{1/2}$, half-wave potential; ^{c)} J , limiting current density.

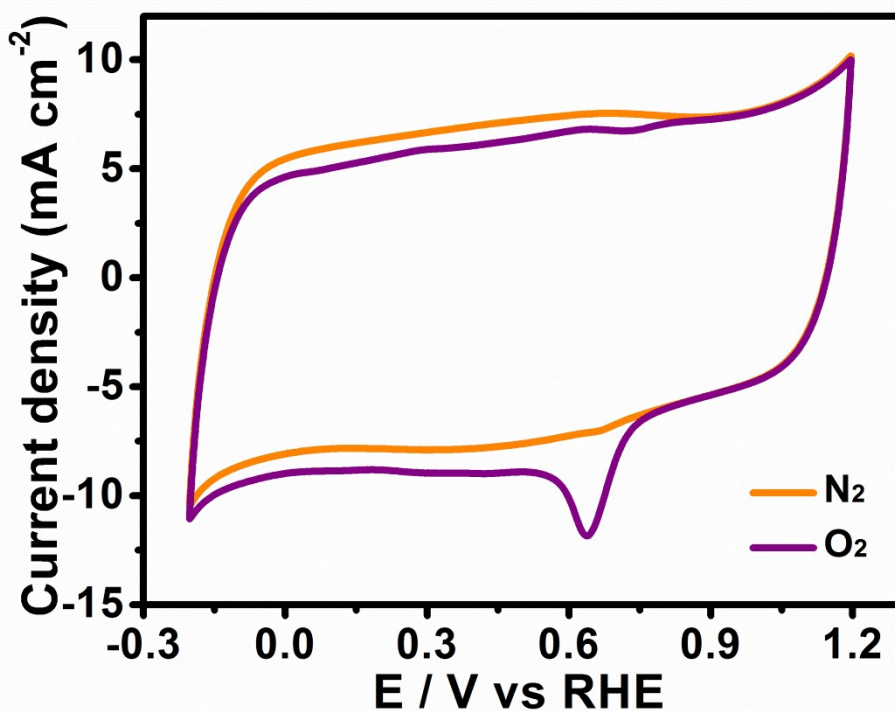


Fig. S8 CVs of CoN₃@NC-7-1000C in N₂- and O₂-saturated 0.5 M H₂SO₄.

Table S2. ORR Electrocatalytic Performance of the Samples.

Sample	medium	E ₀ (V) ^{a)}	E _{1/2} (V) ^{b)}	J (mA cm ⁻²) ^{c)}
Co@NC-3-1000	0.5 M H ₂ SO ₄	0.81	0.72	-1.98
CoN ₃ @NC-5-1000	0.5 M H ₂ SO ₄	0.78	0.69	-4.48
CoN ₃ @NC-7-1000	0.5 M H ₂ SO ₄	0.82	0.72	-5.40
CoN ₃ @NC-9-1000	0.5 M H ₂ SO ₄	0.78	0.70	-3.66
CoN ₃ @NC-10-1000	acid	0.77	0.65	-2.47

a) E₀, onset potential, acquired at an ORR current density of - 0.1 mA cm⁻²; ^{b)}E_{1/2}, half-wave potential; ^{c)}J, limiting current density.

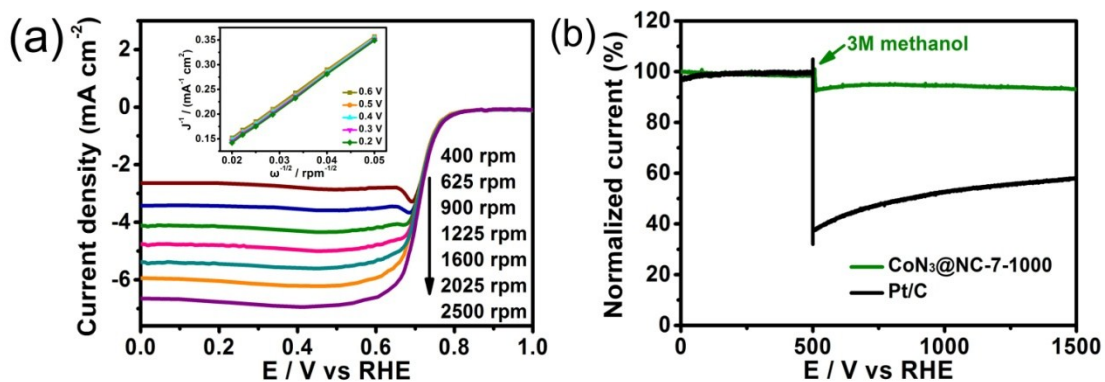


Fig. S9 (a) LSV curves of CoN₃@NC-7-1000 at various rotation speeds. Insert: K-L plots for CoN₃@NC-7-1000 obtained from LSV curves at different electrode potentials. (b) Durability of CoN₃@NC-7-1000 and Pt/C electrode upon addition of 3 M methanol solution into O₂-saturated 0.5 M H₂SO₄ at 0.1 V (added at 500 s).

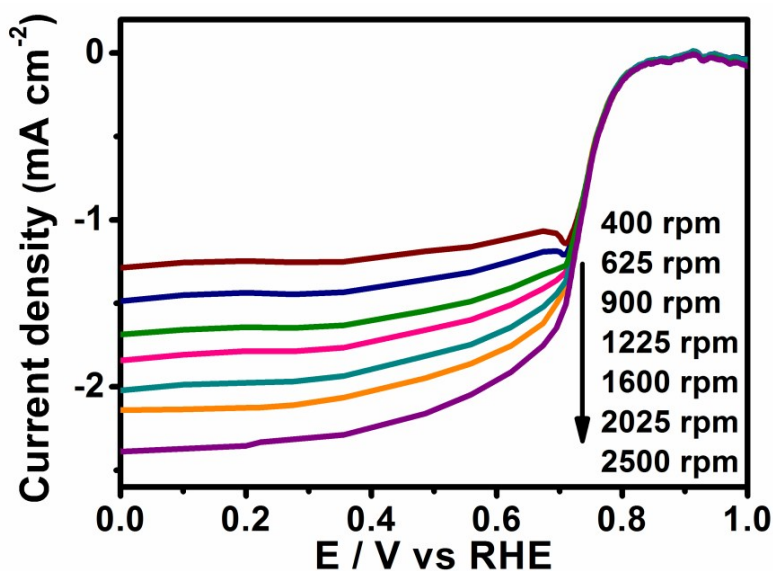


Fig. S10 LSV curves obtained from the RDE test at different speed rate in O₂-saturated 0.5 M H₂SO₄ of Co@NC-3-1000.

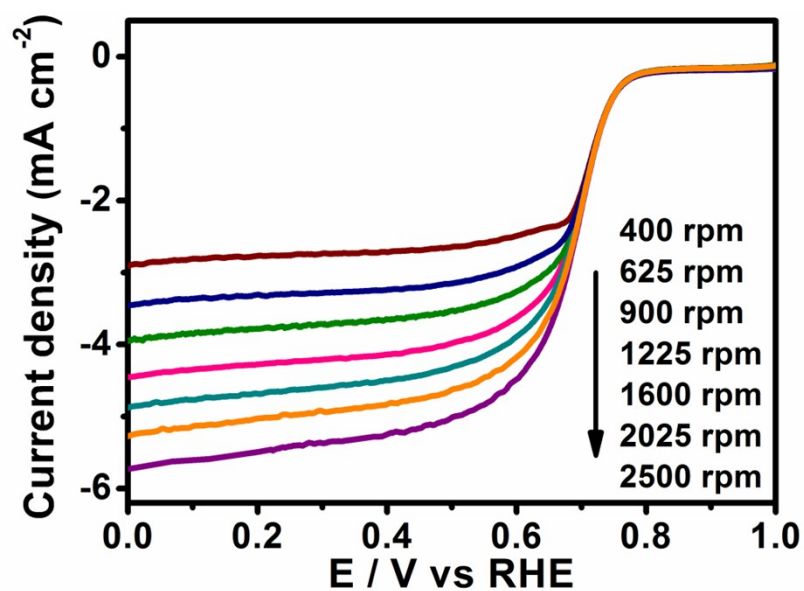


Fig. S11 LSV curves obtained from the RDE test at different speed rate in O₂-saturated 0.5 M H₂SO₄ of CoN₃@NC-5-1000.

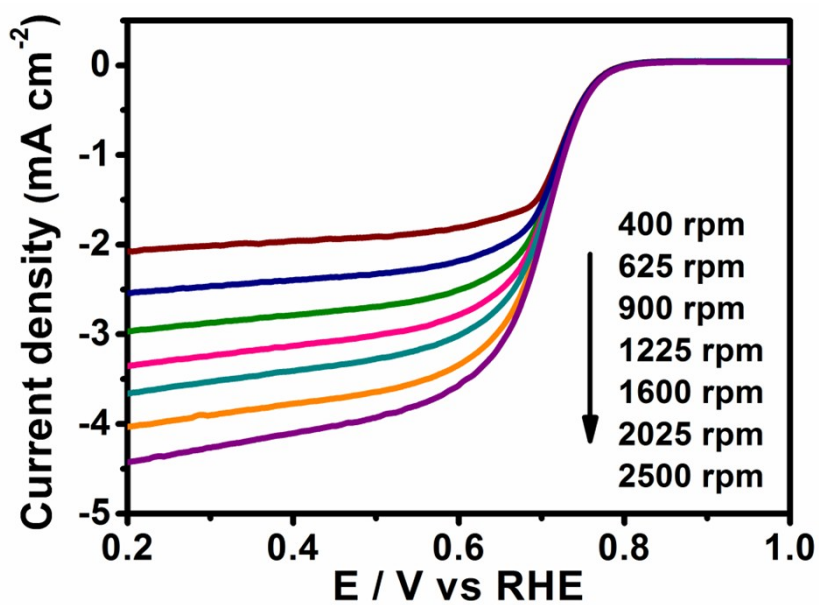


Fig. S12 LSV curves obtained from the RDE test at different speed rate in O₂-saturated 0.5 M H₂SO₄ of CoN₃@NC-9-1000.

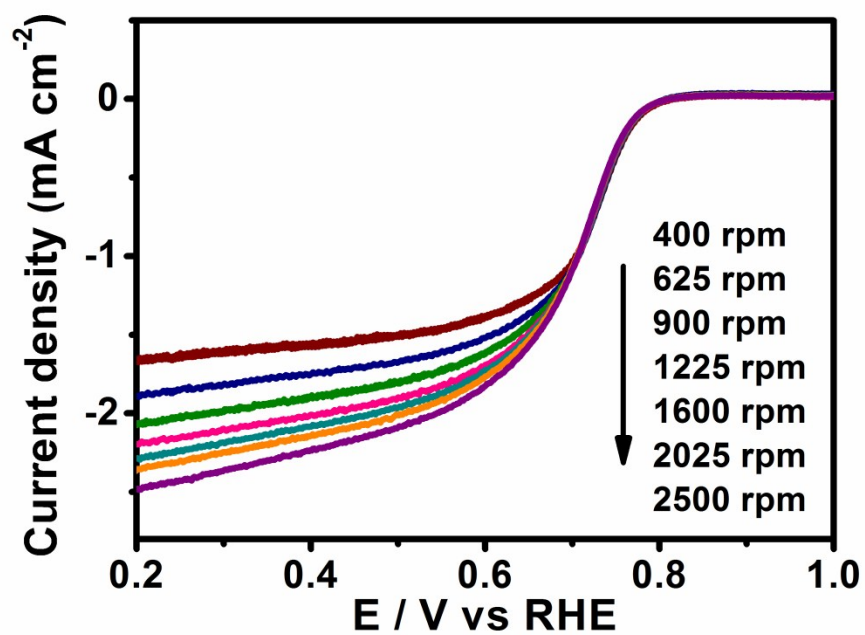


Fig. S13 LSV curves obtained from the RDE test at different speed rate in O₂-saturated 0.5 M H₂SO₄ of Co@NC-10-1000.

References

- 1 Y. Jia, L. Zhang, A. Du, G. Gao, J. Chen, X. Yan, C. Brown, X. Yao, *Adv. Mater.* **2016**, *28*, 9532-9538.