Cobalt decorated nitrogen-doped carbon bowls as efficient electrocatalysts for oxygen reduction reaction

1. Experimental section

Reagents and solutions. All chemicals were of reagent grade and used without further purifications. Tetraethyl orthosilicate (C₈H₂₀O₄Si) and resorcinol (C₆H₆O₂), were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Ammonia hydroxide (NH₃·H₂O), formaldehyde (CH₂O), hydrofluoric acid (HF), cobalt acetate (Co(Ac)₂), and zinc acetate (Zn(Ac)₂) were purchased from Sinopharm Chemical Reagent Co., LTD.

Synthesis of the RF bowls. Initially, 3 mL (20.4 mmol) of ammonia aqueous solution (32 wt%) was added to 80 mL ethanol/water mixture (ethanol/water volume ratio = 7). Then, 0.4 g resorcinol and 2.8 mL tetraethyl orthosilicate were added into the above solution and stirred for 10 minutes at room temperature. Afterwards, 0.56 mL formaldehyde was added into the solution and stirred for 24 hours at room temperature then subsequently at 100 ºC for 24 hours (static conditions). The product was collected by centrifugation, washed with water and ethanol for several times and air-dried at 70 ºC for several hours in an oven. After drying, the silica@RF spheres were obtained. RF bowls were obtained by dissolving the silica with hydrofluoric acid (15 wt%).

Synthesis of the CB and NCB Catalysts. CB was acquired by heating RF bowls under H₂ flowing at 800 ºC (5 ºC/ min) for 2 hours and NCB was acquired by heating RF bowls under NH₃ flowing at 800 ºC (5 ºC/ min) for 2 hours.

Synthesis of the Co@CB and Co@NCB Catalysts. For the fabrication of Co@CB and Co@NCB, 200 mg RF nanobowls were mixed with 20 mg cobalt acetate (Co(Ac)₂) in 15 mL ethanol and stirred at 80 ºC until the ethanol was completely evaporated and then Co-precursor was obtained. Co@CB was acquired by heating the Co-precursor in H₂ flowing at 800 ºC (5 ºC/ min) for 2 hours and Co@NCB was acquired by heating the Co-precursor in NH₃ flowing at 800 ºC (5 ºC/ min) for 2 hours.

Synthesis of the Co@NCB-AT Catalyst. For the fabrication of Co@NCB-AT, 100 mg Co@NCB was soaked in 0.5 M H₂SO₄ then subsequently at 100 ºC for 12 hours. The product was collected by centrifugation, washed with water.
for several times and air-dried at 70 °C for several hours in an oven. After drying, Co@NCB-AT was obtained.

**Characterization.** The obtained samples were measured with a powder X-ray diffractometer (BRUKER/D8 DISCOVER) in a 2 theta range from 10° to 80° at 1° min⁻¹. The morphology of samples was observed through scanning electron microscopy (JSM-7100F). Raman spectra of the samples were obtained by a Raman Spectrometer (HORIBA LabRAM HR Evolution). X-ray photoelectron spectroscopy analysis was performed using an Escalab 250Xi. The nitrogen adsorption-desorption isotherm was measured by using tri star 3020. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) were recorded using a JEOL JEM-2100F STEM/EDS microscope working at 200 kV. High-angle annular dark field scanning TEM (HAADF-STEM) images were obtained by the Titan Cubed Themis G2 300.

**Electrochemical Text.** Firstly, the glass carbon rotating disk electrode (RDE, 0.1964 cm²) and rotating ring disk electrode (RRDE, 0.2475 cm²) were polished with Al₂O₃ slurry, and washed with ultrapure-water and ethanol for several times. For the measurements in 0.1 M KOH solution, the catalyst ink was composed of 5 mg of catalyst, 5 mg VCX-72R, 30 μL of 5% Nafion solution, 30 μL of ultrapure-water and 440 μL of isopropyl alcohol (IPA). 10 μL (12.5 μL) of the catalyst ink was dropped onto RDE (RRDE) for obtaining a catalyst loading of about 0.5 mg cm⁻². Electrochemical measurements were performed by using a CHI 760E workstation. The electrochemical equipment was made up of a three-electrode system: a glassy carbon electrode, a calomel reference electrode, and a Pt plate counter electrode. Cyclic voltammetry (CV) curves were obtained by cycling scan after purging O₂ for 30 minutes at room temperature. Linear sweep voltammograms (LSV) were obtained at an electrode rotation speed of 1600 rpm with a scan rate of 5 mV s⁻¹ in an O₂-saturated solution unless stated otherwise. Koutecky–Levich plots were obtained at different rotating rates. In addition, the electron transfer number \((n)\) can be calculated from the K-L equation:

\[
\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}
\]

\[
B = 0.62nFCD_0^{2/3}V^{-1/6}
\]

where \(J\) is the current density, \(J_K\) is kinetic current density, and \(J_L\) is limiting current density, \(\omega\) is the angular velocity of the disk, \(n\) is the number of electrons transferred per oxygen molecule, \(F\) is the Faraday constant (96485 C mol⁻¹), \(C_0\) is the bulk concentration of O₂ (1.2 × 10⁻⁶ mol cm⁻³), \(D_0\) is the diffusion coefficient of O₂ in 0.1 M KOH (1.9 × 10⁻⁵ cm² s⁻¹), and \(V\) is the
kinematic viscosity of the 0.1 M KOH (0.011 cm$^2$ s$^{-1}$).

The electron transferred number (n) and hydrogen peroxide yields and can be calculated from the following equations:

$$n = 4 \times \frac{I_d}{I_d + \frac{I_r}{I_d}}$$

$$H_2O_2 \% = 200 \times \frac{\frac{I_r}{N}}{I_d + \frac{I_r}{N}}$$

where $I_d$ disk current and $I_r$ is the ring current. The current collection efficiency of the RRDE is $N = 0.37$.

Electrochemical performances in primary zinc-air battery were assembled with hydrophobic carbon fiber cloth loaded with catalyst ink as the air cathode (catalyst ink was prepared as described in ORR test; active material loading is 1 mg cm$^{-2}$; the cathode area is 1 x 1 cm$^2$), metallic zinc plate as the anode, and the electrochemical performances were measured in 6 M KOH using a customized electrochemical cell. Pure O$_2$ was kept flowing into the air cathode throughout the measurements. The polarization curves were collected by LSV with a scan rate of 10 mV s$^{-1}$ and the durability was tested at constant current density of 10 mA cm$^{-2}$ and 200 mA cm$^{-2}$. The electrochemical data was iR corrected ($R_{Co@NCB} = 1.80 \ \Omega$; $R_{PvC} = 1.54 \ \Omega$).
2. Supplemental figures and tables

Fig. S1 (a) SEM image, and (b) TEM image of SiO$_2$@RF.

Fig. S2 (a) SEM image, and (b) TEM image of RFB.

Fig. S3 (a) SEM image, and (b) TEM image of CB.
Fig. S4 (a) SEM image, and (b) TEM image of NCB.

Fig. S5 (a) SEM image, and (b) EDX mappings of Co@NCB-AT.

Fig. S6 (a) SEM image, (b) TEM image (c) HRTEM image, and (d-f) EDX mappings of Co@CB.
Fig. S7 (a) XRD patterns of Co@CB and Co@NCB. (b) Raman spectra for Co@CB and Co@NCB.

Fig. S8 (a) XPS survey spectrum of Co@CB, (b) high-resolution Co2p XPS spectrum of Co@CB.

Fig. S9 Nitrogen adsorption-desorption isotherm and the corresponding BJH pore size distribution of Co@NB (a) and Co@NCB-AT (b).
Fig. S10 Thermogravimetric analysis curves of Co@NCB, Co@CB, and Co@NCB-AT under air atmosphere.

Fig. S11 Effect of SCN⁻ on ORR activity for Co@NCB catalyst in O₂-saturated 0.1 M KOH electrolyte at the rotating speed of 1600 rpm with the scan rate of 5 mV s⁻¹.
Fig. S12 (a) LSV curves of Co@NCB and Pt/C in O$_2$-saturated 0.1 M HClO$_4$ at 5 mV·s$^{-1}$ and 1600 rpm. (b) Current–time chronoamperometric responses of Co@NCB and Pt/C in O$_2$-saturated 0.1 M HClO$_4$ at 0.40 V and 1225 rpm. (c) RDE polarization curves of Co@NCB in O$_2$-saturated 0.1 M KOH with various rotation rates at a scan rate of 5 mV s$^{-1}$. (d) Koutecky–Levich plots of Co@NCB at different potentials.

Fig. S13 Percentage of peroxide and electron transfer number of Co@NCB, inset: corresponding RRDE curves in 0.1 M KOH at a rotating rate of 1600 rpm.
Table S1. Comparison of the ORR activity of Co@NCB with previously reported Co-based catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$E_{1/2}$, V vs. RHE (0.1 M KOH)</th>
<th>Ref</th>
</tr>
</thead>
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<tr>
<td>Co@NC</td>
<td>0.79</td>
<td>[1]</td>
</tr>
<tr>
<td>Co-N-C nanofiber</td>
<td>0.78</td>
<td>[2]</td>
</tr>
<tr>
<td>Co-N-C</td>
<td>0.87</td>
<td>[3]</td>
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<tr>
<td>Co/NC</td>
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<td>[4]</td>
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<tr>
<td>Co$_3$ZnN/N-CB</td>
<td>0.829</td>
<td>[5]</td>
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<tr>
<td>Co-N/CNFs</td>
<td>0.82</td>
<td>[6]</td>
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<tr>
<td>Co/N-CNTs</td>
<td>0.84</td>
<td>[7]</td>
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<tr>
<td>Co-doped ZIFs</td>
<td>0.85</td>
<td>[8]</td>
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<tr>
<td>MOFs-800</td>
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<td>[9]</td>
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<tr>
<td>Co 16%-NCNT-T800</td>
<td>0.846</td>
<td>[10]</td>
</tr>
<tr>
<td>Co@NCB</td>
<td>0.851</td>
<td>this work</td>
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