

## Electronic Supplementary Information

### 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 ( $C_8H_{20}O_4Si$ ) and resorcinol ( $C_6H_6O_2$ ), were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Ammonia hydroxide ( $NH_3 \cdot H_2O$ ), formaldehyde ( $CH_2O$ ), 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 °C for 24 hours (static conditions). The product was collected by centrifugation, washed with water and ethanol for several times and air-dried at 70 °C 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  $H_2$  flowing at 800 °C (5 °C/ min) for 2 hours and NCB was acquired by heating RF bowls under  $NH_3$  flowing at 800 °C (5 °C/ 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 °C until the ethanol was completely evaporated and then Co-precursor was obtained. Co@CB was acquired by heating the Co-precursor in  $H_2$  flowing at 800 °C (5 °C/ min) for 2 hours and Co@NCB was acquired by heating the Co-precursor in  $NH_3$  flowing at 800 °C (5 °C/ 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  $H_2SO_4$  then subsequently at 100 °C 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<sup>-1</sup>. 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 II. 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 cm<sup>2</sup>) and rotating ring disk electrode (RRDE, 0.2475 cm<sup>2</sup>) were polished with Al<sub>2</sub>O<sub>3</sub> 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<sup>-2</sup>. 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 O<sub>2</sub> 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<sup>-1</sup> in an O<sub>2</sub>-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:

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

$$B = 0.62nFC_0D_0^{2/3}V^{-1/6}$$

where *J* is the current density, *J<sub>K</sub>* is kinetic current density, and *J<sub>L</sub>* 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<sup>-1</sup>), *C<sub>0</sub>* is the bulk concentration of O<sub>2</sub> (1.2 × 10<sup>-6</sup> mol cm<sup>-3</sup>), *D<sub>0</sub>* is the diffusion coefficient of O<sub>2</sub> in 0.1 M KOH (1.9 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>), and *V* is the

kinematic viscosity of the 0.1 M KOH ( $0.011 \text{ cm}^2 \text{ s}^{-1}$ ).

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

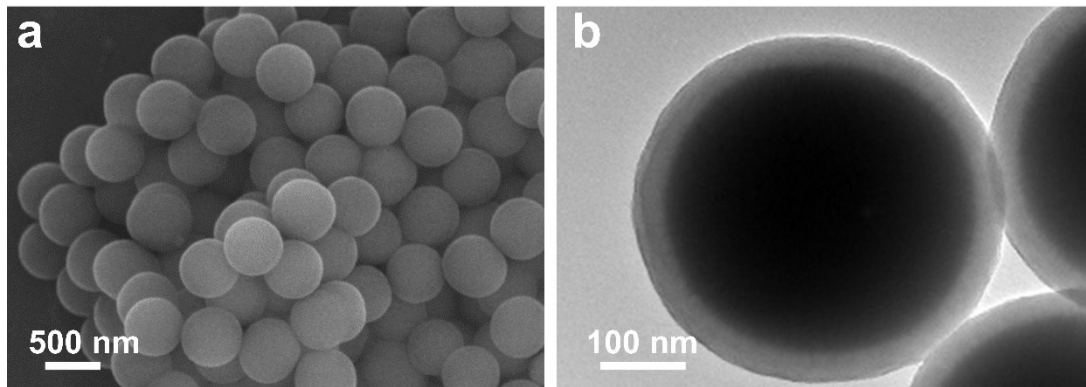
$$n = 4 \times \frac{I_d}{I_d + \frac{I_r}{N}}$$

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

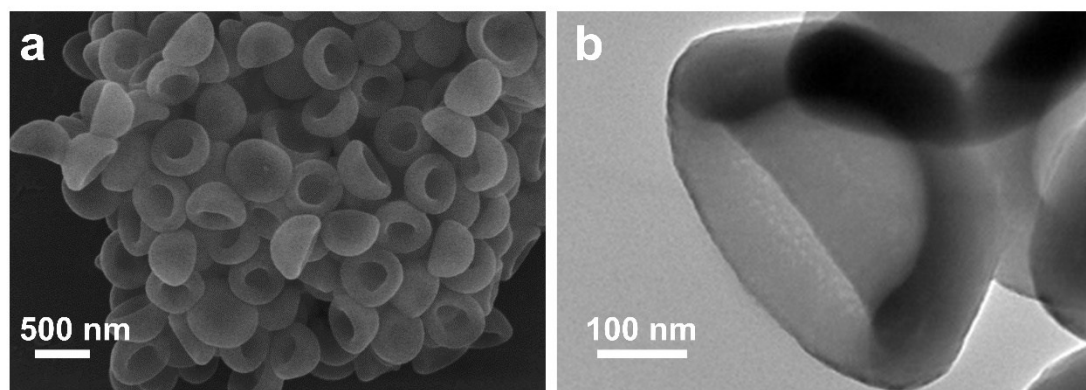
where  $I_d$  disk current and  $I_r$  is the ring current. The current collection efficiency of the RRDE is  $N = 0.37$ .

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  $1 \text{ mg cm}^{-2}$ ; the cathode area is  $1 \times 1 \text{ cm}^2$ ), 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  $10 \text{ mV s}^{-1}$  and the durability was tested at constant current density of  $10 \text{ mA cm}^{-2}$  and  $200 \text{ mA cm}^{-2}$ . The electrochemical data was  $iR$  corrected ( $R_{Co@NCB} = 1.80 \Omega$ ;  $R_{PVC} = 1.54 \Omega$ ).

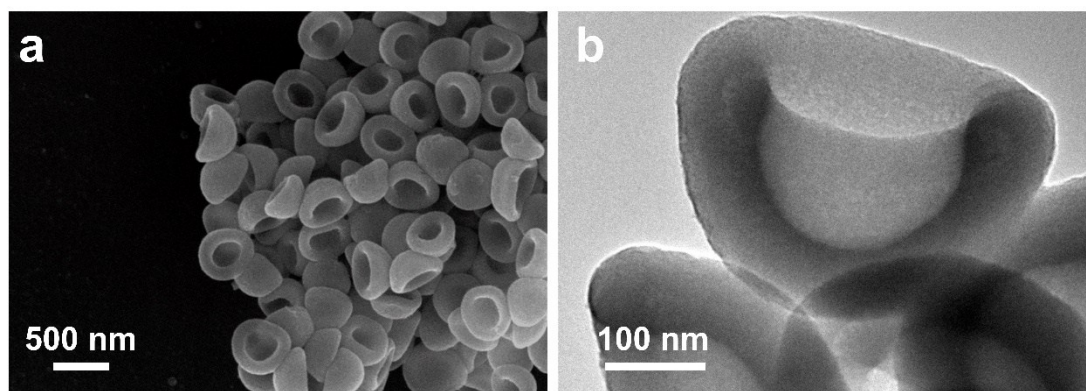
## 2. Supplemental figures and tables



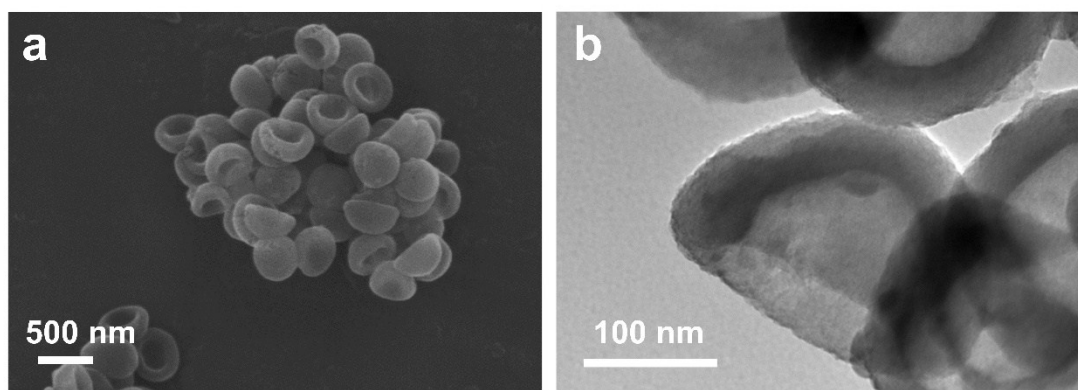
**Fig. S1** (a) SEM image, and (b) TEM image of  $\text{SiO}_2\text{@RF}$ .



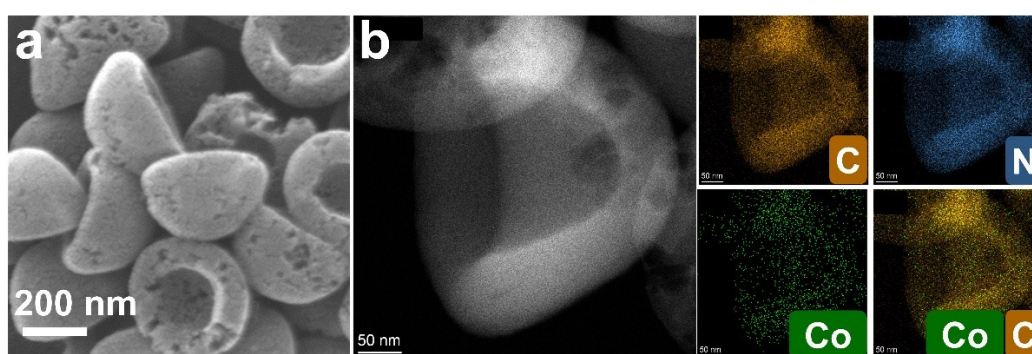
**Fig. S2** (a) SEM image, and (b) TEM image of RFB.



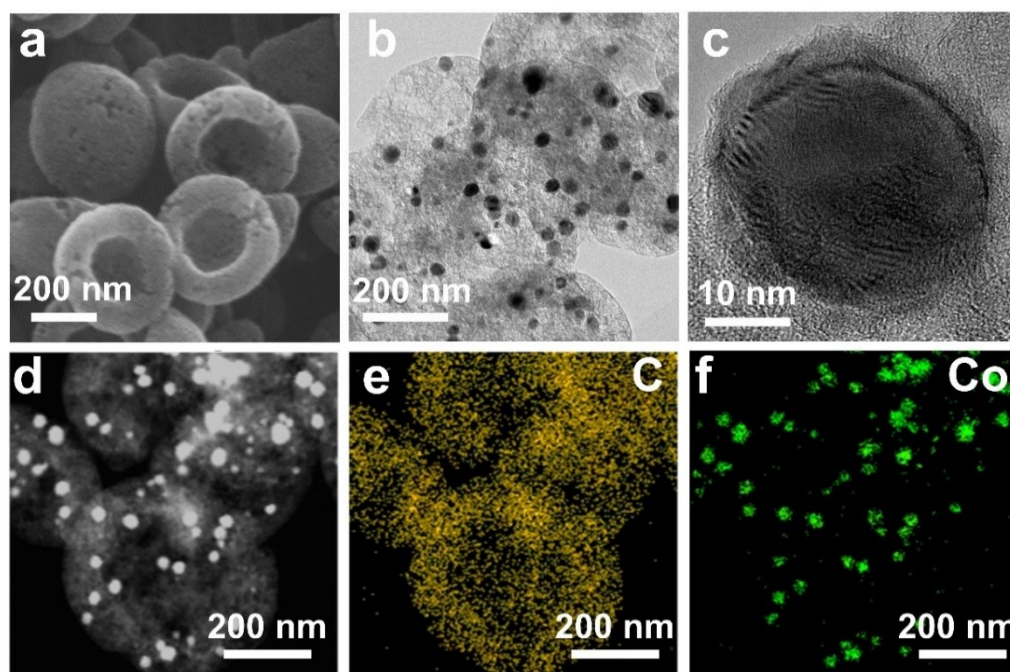
**Fig. S3** (a) SEM image, and (b) TEM image of CB.



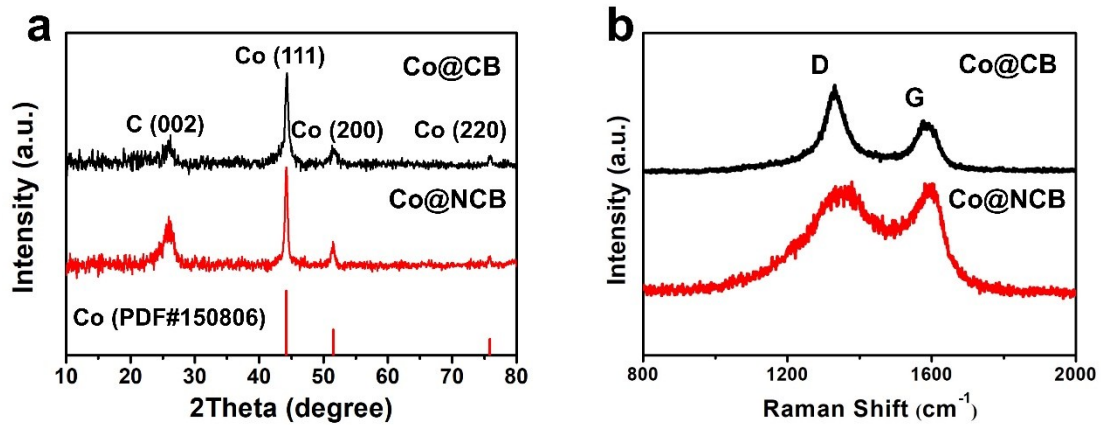
**Fig. S4** (a) SEM image, and (b) TEM image of NCB.



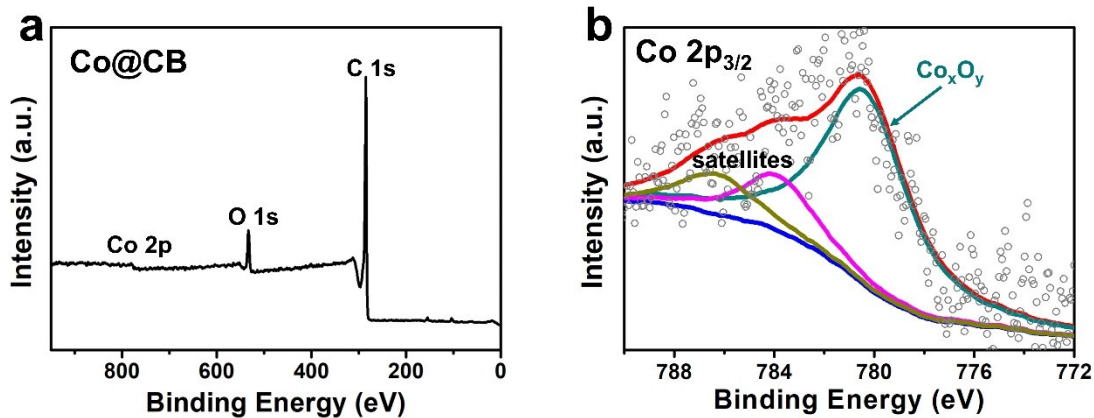
**Fig. S5** (a) SEM image, and (b) EDX mappings of Co@NCB-AT.



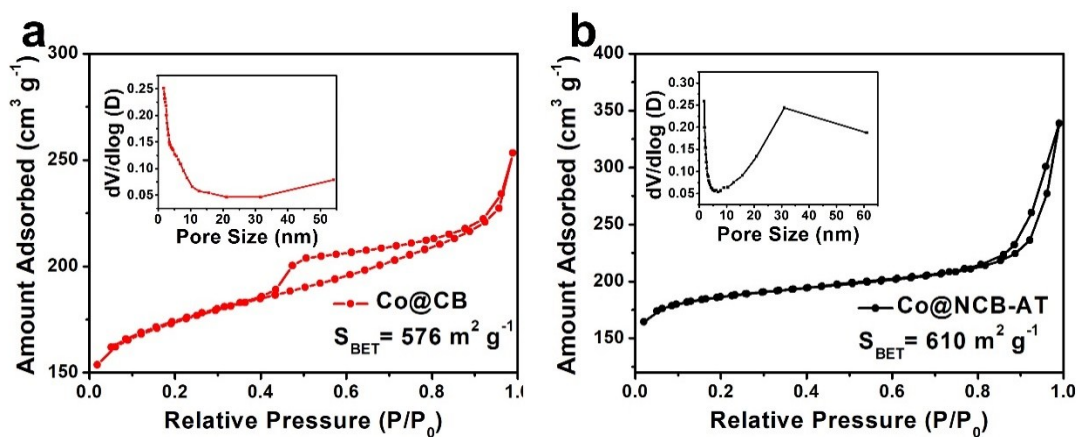
**Fig. S6** (a) SEM image, (b) TEM image (c) HRTEM image, and (d-f) EDX mappings of Co@CB.



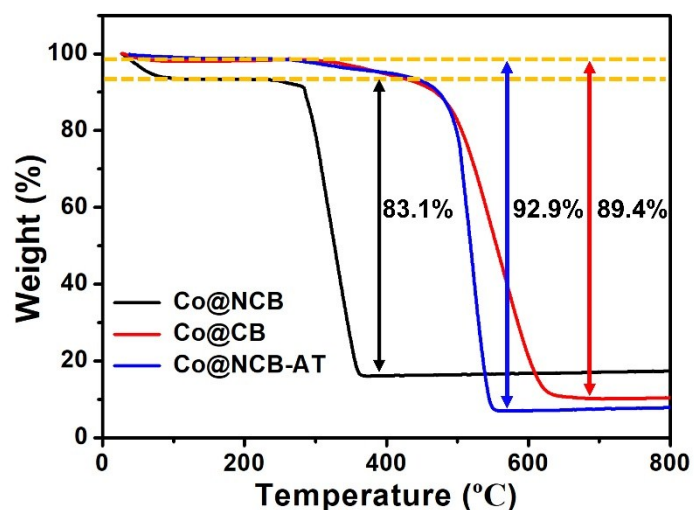
**Fig. S7** (a) XRD patterns of Co@CB and Co@NCB. (b) Raman spectra for Co@CB and Co@NCB.



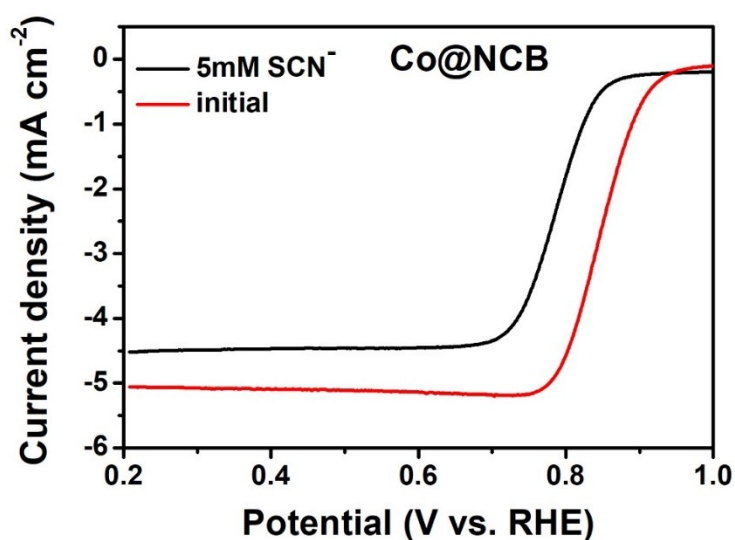
**Fig. S8** (a) XPS survey spectrum of Co@CB, (b) high-resolution Co2p XPS spectrum of Co@CB.



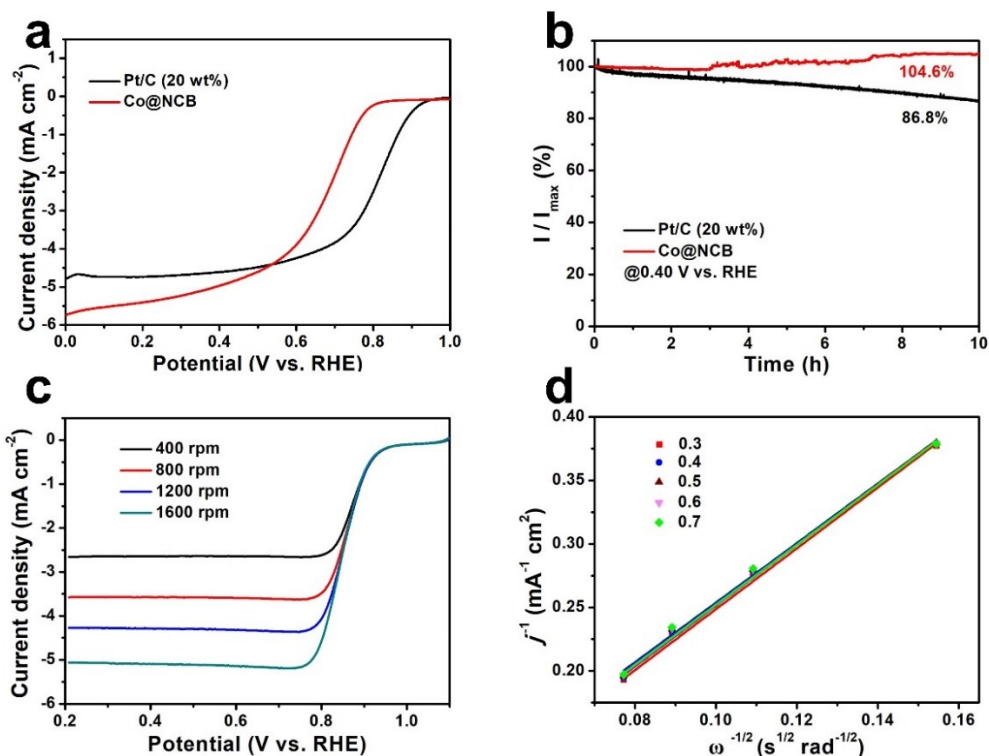
**Fig. S9** Nitrogen adsorption-desorption isotherm and the corresponding BJH pore size distribution of Co@NB (a) and Co@NCB-AT (b).



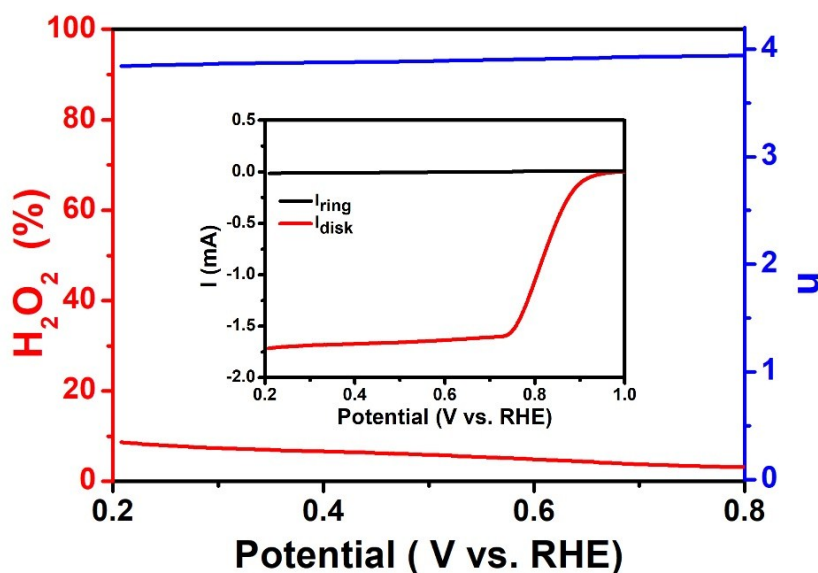
**Fig. S10** Thermogravimetric analysis curves of Co@NCB, Co@CB, and Co@NCB-AT under air atmosphere.



**Fig. S11** Effect of  $\text{SCN}^-$  on ORR activity for Co@NCB catalyst in  $\text{O}_2$ -saturated 0.1 M KOH electrolyte at the rotating speed of 1600 rpm with the scan rate of  $5 \text{ mV s}^{-1}$ .



**Fig. S12** (a) LSV curves of Co@NCB and Pt/C in  $O_2$ -saturated 0.1 M  $HClO_4$  at  $5\text{ mV}\cdot\text{s}^{-1}$  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  $5\text{ mV s}^{-1}$ . (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.

Catalysts	$E_{1/2}$ , V vs. RHE (0.1 M KOH)	Ref
Co@NC	0.79	[1]
Co-N-C nanofiber	0.78	[2]
Co-N-C	0.87	[3]
Co/NC	0.83	[4]
Co <sub>3</sub> ZnN/N-CB	0.829	[5]
Co-N/CNFs	0.82	[6]
Co/N-CNTs	0.84	[7]
Co-doped ZIFs	0.85	[8]
MOFs-800	0.80	[9]
Co 16%-NCNT-T800	0.846	[10]
Co@NCB	0.851	this work

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