Supplementary information

Bimetallic ZIF Derived Co Nanoparticles anchored N-doped porous carbons for Efficient Oxygen Reduction Reaction

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Experimental Section

Materials

All the chemicals in this experiment were directly commercially available and had not undergone any purification. Zinc nitrate hexahydrate (98%, Sigma-Aldrich), Cobalt hexahydrate (99%, Aladdin, AR), Benzimidazole (99%, Alfa Aesar), 2-methylbenzimidazole (98%, Sigma-Aldrich), commercial catalyst Pt/C (20 wt% metal, Hispec 3000 Johnson Matthey). *N,N′*-dimethylformamide (DMF) and Methanol (CH_3OH) were both from the West Long Chemical Co., Ltd.

Synthesis of ZnCo-JUC160 precursors

Synthesis of Zn_3Co_1-JUC160

0.8 mmol of 2-methylbenzimidazole and 1 mmol of benzimidazole were stirred and dispersed in DMF (12 ml) solution. Then $Zn(NO_3)_2•6H_2O$ (0.6 mmol) and $Co(NO_3)_2•6H_2O$ (0.2 mmol) was ultrasonically dissolved in the 12 ml DMF solution. Followed by the mixture solution of zinc hexahydrate and cobalt hexahydrate was added to the solution containing benzimidazole and 2-methylbenzimidazole drop by drop, and stirring was continued for 1 h. Then poured the mixed solution into a polytetrafluoroethylene reactor and reacted at 180 °C for 48 h. Waiting for cooling to ambient temperature, the final product was obtained by suction filtration, washed several times with DMF and methanol. Then placed in a 60 °C oven to dry overnight.

Synthesis of Zn_2Co_1-JUC160

The synthesis process of Zn_2Co_1-JUC160 was generally consistent with the above method, except that the amount of metal was changed, which used $Zn(NO_3)_2•6H_2O$ (0.53 mmol) and $Co(NO_3)_2•6H_2O$ (0.27 mmol) as the metal source.

Synthesis of Zn_1Co_1-JUC160

The synthesis process of Zn_1Co_1-JUC160 was generally consistent with the above method, except that the amount of metal was changed, which used $Zn(NO_3)_2•6H_2O$ (0.40 mmol) and $Co(NO_3)_2•6H_2O$ (0.40 mmol) as the metal source.

Synthesis of Zn_1Co_2-JUC160

The synthesis process of Zn_1Co_2-JUC160 was generally consistent with the above method, except that the amount of metal was changed, which used $Zn(NO_3)_2•6H_2O$ (0.27 mmol) and $Co(NO_3)_2•6H_2O$ (0.53 mmol) as the metal source.

Synthesis of Zn_1Co_3-JUC160

The synthesis process of Zn_1Co_3-JUC160 was generally consistent with the above method, except that the amount of metal was changed, which used $Zn(NO_3)_2•6H_2O$ (0.20 mmol) and $Co(NO_3)_2•6H_2O$ (0.60 mmol) as the metal source.

Synthesis of ZnCo-NPs@NC materials

Synthesis of Zn_3Co_1-NPs@NC

About 500 mg of Zn_3Co_1-JUC160 precursor was laid flat in a clean ceramic boat and placed in a tube furnace. Followed by a 30 min intake of Ar atmosphere to exhaust the air. In the Ar atmosphere, the tube furnace was heated at a temperature increase rate of 5 ° C/min and the sample was continuously annealed at 950 ° C for 2 h. Waiting until it reached room temperature, a Co anchored N-doped porous carbon material was obtained and then soaked the materials with 0.5M sulfuric acid in the oven at 80 °C to remove excess impurities and finally got Zn_3Co_1-NPs@NC.

Synthesis of Zn_2Co_1-NPs@NC

Zn_2Co_1-NPs@NC was synthesised by a carbonization procedure and conditions similar to the above, except that 500 mg Zn_2Co_1-JUC160 was used as the precursor.

Synthesis of Zn_1Co_1-NPs@NC

Zn_1Co_1-NPs@NC was synthesised by a carbonization procedure and conditions similar to the above, except that 500 mg Zn_1Co_1-JUC160 was used as the precursor.

Synthesis of Zn_1Co_2-NPs@NC

Zn_1Co_2-NPs@NC was synthesised by a carbonization procedure and conditions similar to the above, except that 500 mg Zn_1Co_2-JUC160 was used as the precursor.

Synthesis of Zn_1Co_3-NPs@NC

Zn_1Co_3-NPs@NC was synthesised by a carbonization procedure and conditions similar to the above, except that 500 mg Zn_1Co_3-JUC160 was used as the precursor.

Synthesis of Zn_2Co_1-NPs@NC-800, Zn_2Co_1-NPs@NC-900, Zn_2Co_1-NPs@NC-1000 and Zn_2Co_1-NPs@NC-1100

The Zn_2Co_1-JUC160 precursors were weighed into a clean ceramic boat and placed into a tube furnace. Followed by a 30min intake of Ar atmosphere to exhaust the air. Then, in the Ar atmosphere, the samples were respectively annealed at 800, 900, 1000 and 1100 °C for 2h at the heating rate of 5 °C per minute. Then soaked the materials with 0.5M sulfuric acid in the oven at 80 °C to remove excess impurities and finally got Zn_2Co_1-NPs@NC-800, Zn_2Co_1-NPs@NC-900, Zn_2Co_1-NPs@NC-1000 and Zn_2Co_1-NPs@NC-1100.

Characterization

The phase of samples was investigated by Powder X-ray diffraction (PXRD) using Cu-Kα radiation ($\lambda = 1.5418$ Å) of SHIMADZU LabX XRD-6000diffractometer at 35 kV, 25 mA. The degree of graphitization of the samples was recorded by Raman spectra with a Lab RAM HR800 Raman spectrometer and the samples were excited by a 532 nm from an argon-ion laser. X-ray photoelectron spectroscopy (XPS) spectra were conducted on an ESCALAB250 spectrometer. Inductively coupled plasma (ICP) analyses were recorded by a Perkin-Elmer Optima 3300DV spectrometer. The microscopic morphologies and sizes of all samples were characterized by the scanning electron microscopy (SEM) image using a JEOS JSM-6510 system. Transmission electron microscopy (TEM) images were carried on a JEM-2100 microscope which recorded by using a Gatan 794CCD camera. A small number of samples were dispersed in the ethanol solution and coated in carbon film drops. Both the surface area and pore diameter distribution information of the materials were obtained by N_2 sorption analysis measured at 77K using a Quantachrome Autosorb-iQ MP gas sorptometer. The as-prepared materials were activated with a turbo molecular vacuum pump at 180 °C for 12 h before testing. Finally, based on nitrogen adsorption data, the surface areas of the materials were calculated by Brunauer–Emmett–Teller (BET) method and the pore size distribution was obtained by Non-Localized Density Functional Theory (NLDFT) method. Thermogravimetric analysis (TGA) was tested on a SHIMADZU DTG-60thermal analyser system at a heating rate of 10°C/ min from 25 to 950 °C under dry air.

Electrochemical measurements

The electrocatalytic characterization toward ORR was recorded by an electrochemical workstation (CHI760E, Shanghai Chenhua Instruments Co.). All electrocatalytic performance of samples was detected in a 0.1 M KOH electrolyte at room temperature with a three-electrode system, where Ag/AgCl used as the reference electrode, platinum wire as the counter electrode and the rotating ring-disk glass carbon with the catalyst of 3mm disk diameter as the working electrode. In a typical process to make up the electrode ink, 3 mg of catalyst powder was suspended in a mixed solvent containing 30 uL of 5 wt % Nafion solution, 150 uL of deionized water and 150 uL of C_2H_5OH. Later, the suspension was placed in an ultrasonic bath to form a homogeneous catalyst ink. Then 6uL ink prepared by the above method was evenly covered on the GC electrode and naturally dried at the ambient condition with a catalyst mass loading of about 0.772 mg cm^2. As a control, a 20 wt % Pt/C catalyst was prepared with the mass loading of about 0.386 mg cm^2. The entire test procedure was to test Cyclic voltammograms (CV) with a sweep rate of 50 mV s^{-1} and LSV under nitrogen or oxygen saturation, respectively. Before every test, the 0.1 M KOH electrolyte was pre-purged with pure O_2 for 30 min to make sure it was O_2-saturated. During testing, oxygen gas maintained flow. Firstly, the material was activated by scanning the CV curve multiple times until the CV curve coincided, indicating that the test was in a stable state. The linear sweep voltammetry (LSV) curves with a scan rate of 10 mV s^{-1} of the materials were then tested at different rotational rates of 400, 625, 1225, 1600, 2025, 2500, respectively. The long-term durability of the materials was demonstrated by testing the stability of the current over time at a fixed voltage of 0.6 V at 1600 rpm in an oxygen-saturated electrolyte. All recorded potentials during the experiment were converted to a RHE according to the following formula: *E* (versus RHE) = *E* (versus Ag/AgCl) + 0.197 + 0.059 pH. The electrochemical surface area was determined by using the in situ method based on the measurement of electrochemical double-layer capacitance in the non-Faradaic potential region.

The electron transfer numbers (n) per oxygen molecule during oxygen reduction were calculated with the Koutecky–Levich (K–L) equation:

$$J^{-1} = J_k^{-1} + \left(0.62nFCD^{2/3}\gamma^{-1/6}\omega^{1/2}\right)^{-1}$$

where J and J_k represent the measured current density and kinetic current density, respectively. ω is the electrode rotation rate, n refers to the electron transfer number, F is the Faraday constant, C represents the O_2 saturation concentration in the electrolyte, D is the O_2 diffusion coefficient in the electrolyte, and Υ refers to the kinetic viscosity of the electrolyte.

Table S1. the molar ratio of Zn/Co in **ZnCo-JUC160** precursor and Quantitative analysis of the Zn/Co ratio in products by ICP and EDS.

Sample	Zn/Co ratio in reactants	Zn/Co ratio in products	
		EDS	ICP
Zn_3Co_1-JUC160	3:1	3.35:1	3.22:1
Zn_2Co_1-JUC160	2:1	2.19:1	2.07:1
Zn_1Co_1-JUC160	1:1	1:1.1	1.06:1
Zn_1Co_2-JUC160	1:2	1:2.08	1:2.14
Zn_1Co_3-JUC160	1:3	1:3.2	1:2.95

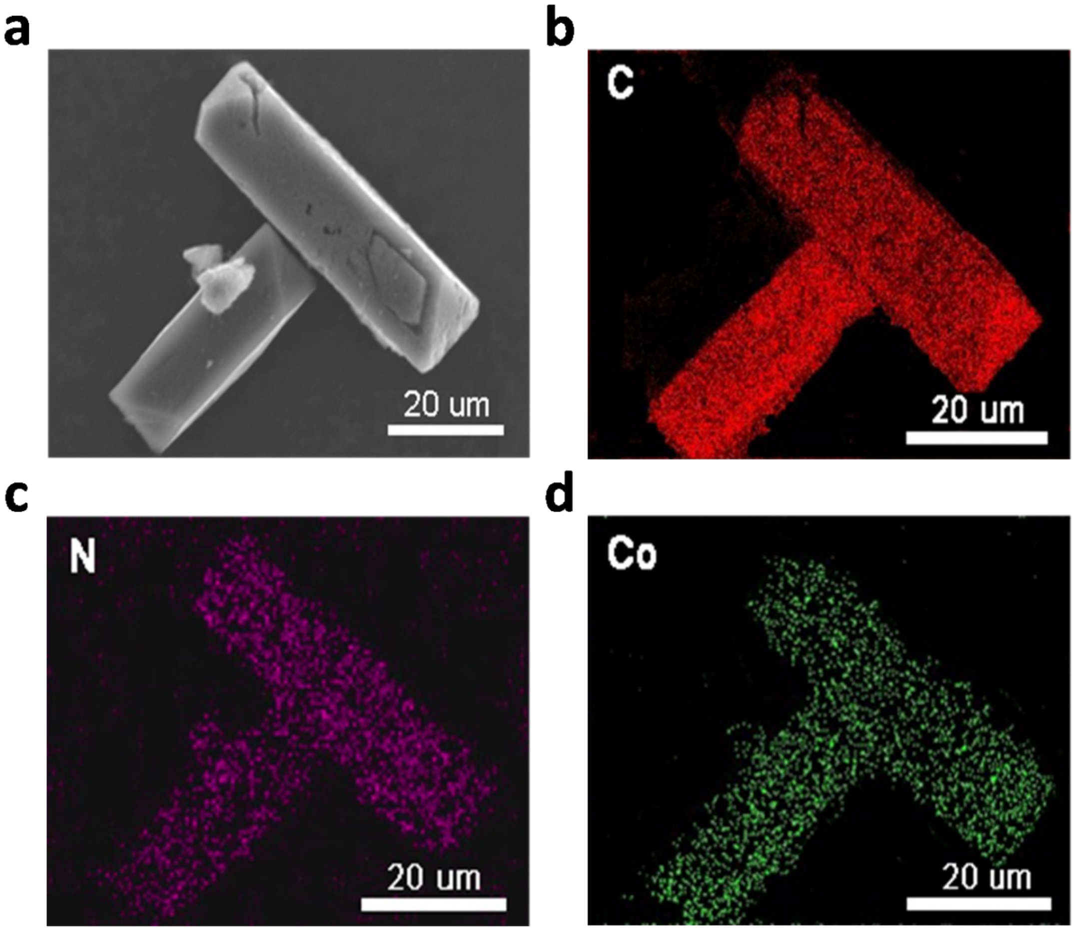

Figure.S1 (a) SEM image of **Zn_2Co_1-NPs@NC** material, EDS mappings of the (b) C element, (c) N element and (d) Co element in **Zn_2Co_1-NPs@NC** material.

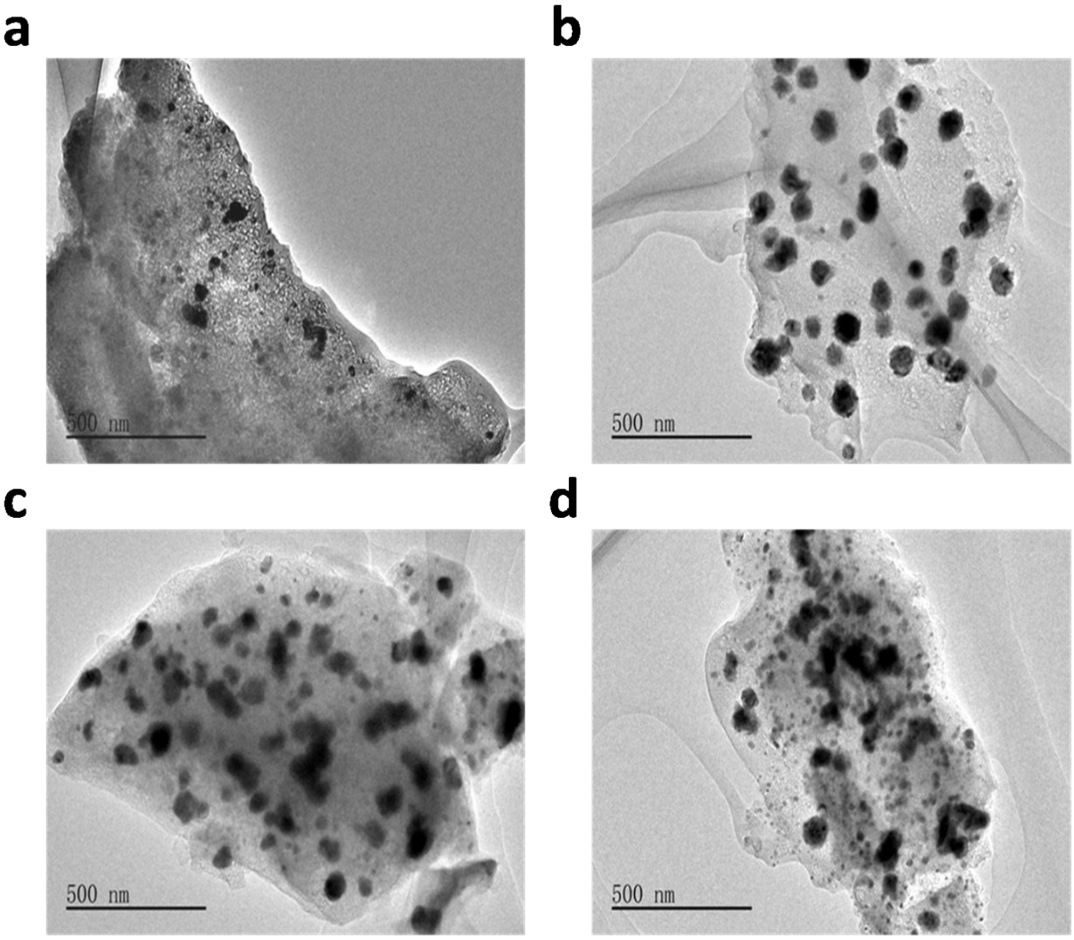

Figure. S2 The TEM images of (a) **Zn_3Co_1-NPs@NC**,(b) **Zn_1Co_1-NPs@NC**, (c) **Zn_1Co_2-NPs@NC** and (d) **Zn_1Co_3-NPs@NC**.

Table S2. Structure parameters of the prepared **ZnCo-NPs@NC** materials.

Samples	S_{BET} [a] (m^2g^{-1})	V_{total} [b] (cm^3g^{-1})	V_{micro} [c] (cm^3g^{-1})	D_{pore} [d] (nm)	Co Cotent (wt%)
Zn_3Co_1-NPs@NC	500.4	0.32	0.12(39)	0.67	9.9
Zn_2Co_1-NPs@NC	406.7	0.28	0.09(87)	0.64	12.99
Zn_1Co_1-NPs@NC	400.1	0.26	0.17(79)	0.70	17.41
Zn_1Co_2-NPs@NC	372.8	0.26	0.09(28)	0.64	16.91
Zn_1Co_3-NPs@NC	355.1	0.27	0.08(36)	0.59	21.8

[a] S_{BET} estimated in the relative pressure from 0.05 to 0.20 bar, which gives the best linearity. [b] Total (micro- and meso-) pore volume at the relativepressure $P/P_0 = 0.99$. [c] Cumulative micropore volume with pore size ≤2 nm, the values in brackets are the percentage of micropore volume to totalpore volume. [d] The median pore size calculated by the Horvath–Kawazoe (HK) method.

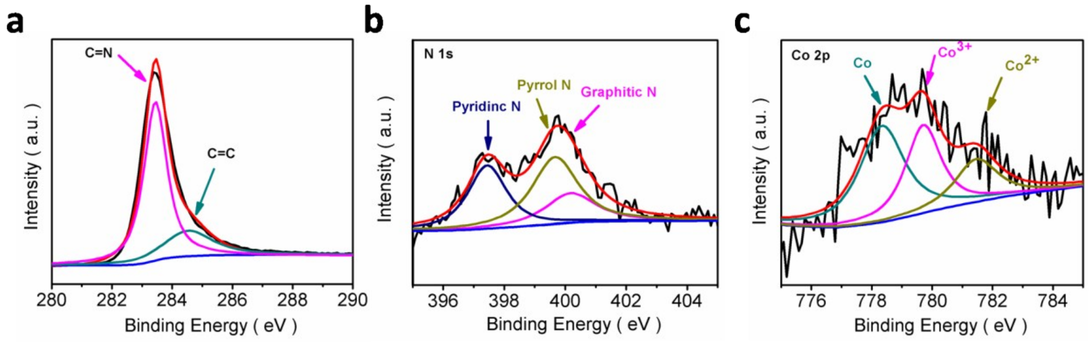

Fig. S3 High-resolution XPS spectra of **Zn_2Co_1-NPs@NC**: (a) C 1s, (b) N 1s, (c) Co 2p.

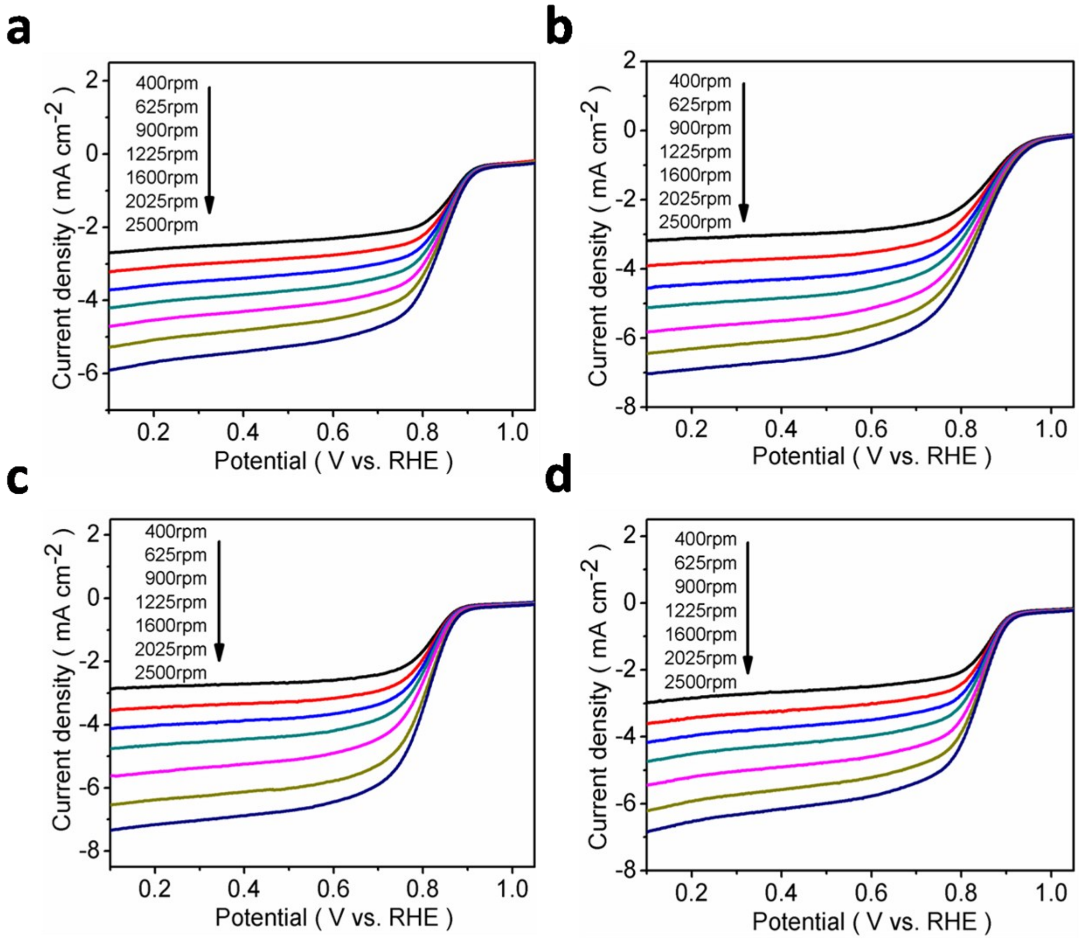

Fig. S4 LSV curves of **Zn_3Co_1-NPs@NC, Zn_1Co_1-NPs@NC, Zn_1Co_2-NPs@NC** and **Zn_1Co_3-NPs@NC** from 400 to 3025 rpm in O_2-saturated 0.1M KOH conditions at room temperature.

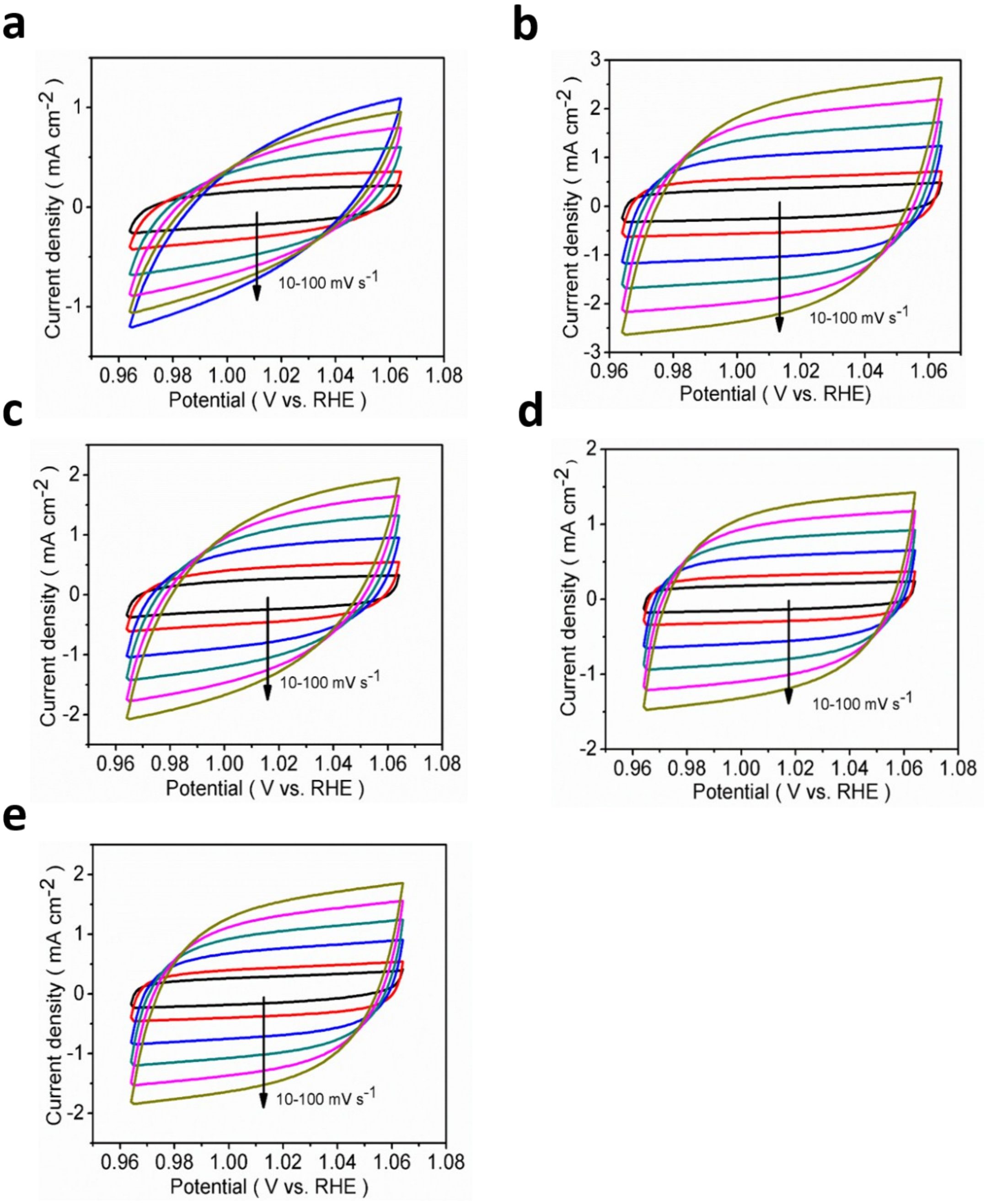

Fig.S5 Cyclic Voltammograms of the(a) **Zn_3Co_1-NPs@NC**, (b) **Zn_2Co_1-NPs@NC**, (c) **Zn_1Co_1-NPs@NC**, (d) **Zn_1Co_2-NPs@NC** and (e) **Zn_1Co_3-NPs@NC** at various scan rates (10, 20, 40, 60, 80, and 100 mV s^{-1}) in 0.1 M KOH. (f) The estimated electrochemical double-layer capacitance (Cdl).

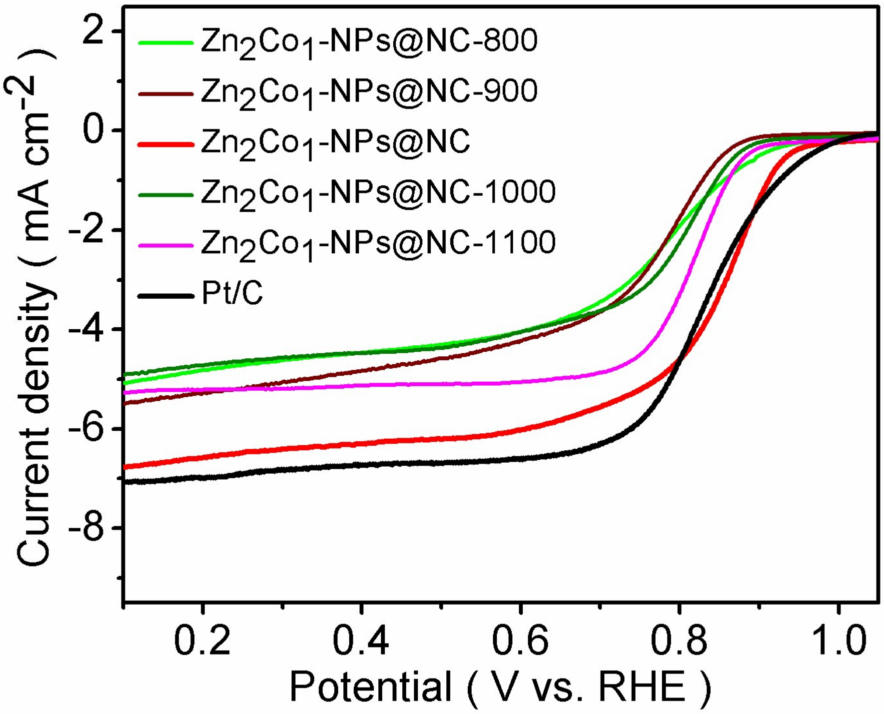

Fig. S6 Linear sweep voltammetry (LSV) curves at 1600 rpm of **Zn_2Co_1-NPs@NC-800**, **Zn_2Co_1-NPs@NC-900**, **Zn_2Co_1-NPs@NC-1000** and **Zn_2Co_1-NPs@NC-1100.**

Notes: The content of metal Co was calculated by thermogravimetric analysis of carbonized samples in dry air. After carbonization at 950℃, the remaining elements in the samples were C, N, O and Co, in which C and N elements were oxidized to CO_2 and NO_2 respectively and disappeared with the air flow. Similarly, Co was oxidized to Co_3O_4, that is, the residual material after thermogravimetric analysis was Co_3O_4.

The total mass of the sample before thermogravimetric analysis was recorded as **m**.

The mass of the sample after thermogravimetric analysis was denoted as $\mathbf{m_{Co3O4}}$.

the mass of Co calculated based on the mass of Co_3O_4 was denoted as $\mathbf{m_{Co}}$.

Finally, the content of Co was denoted as **M** = $\mathbf{m_{Co}}$ / **m**.

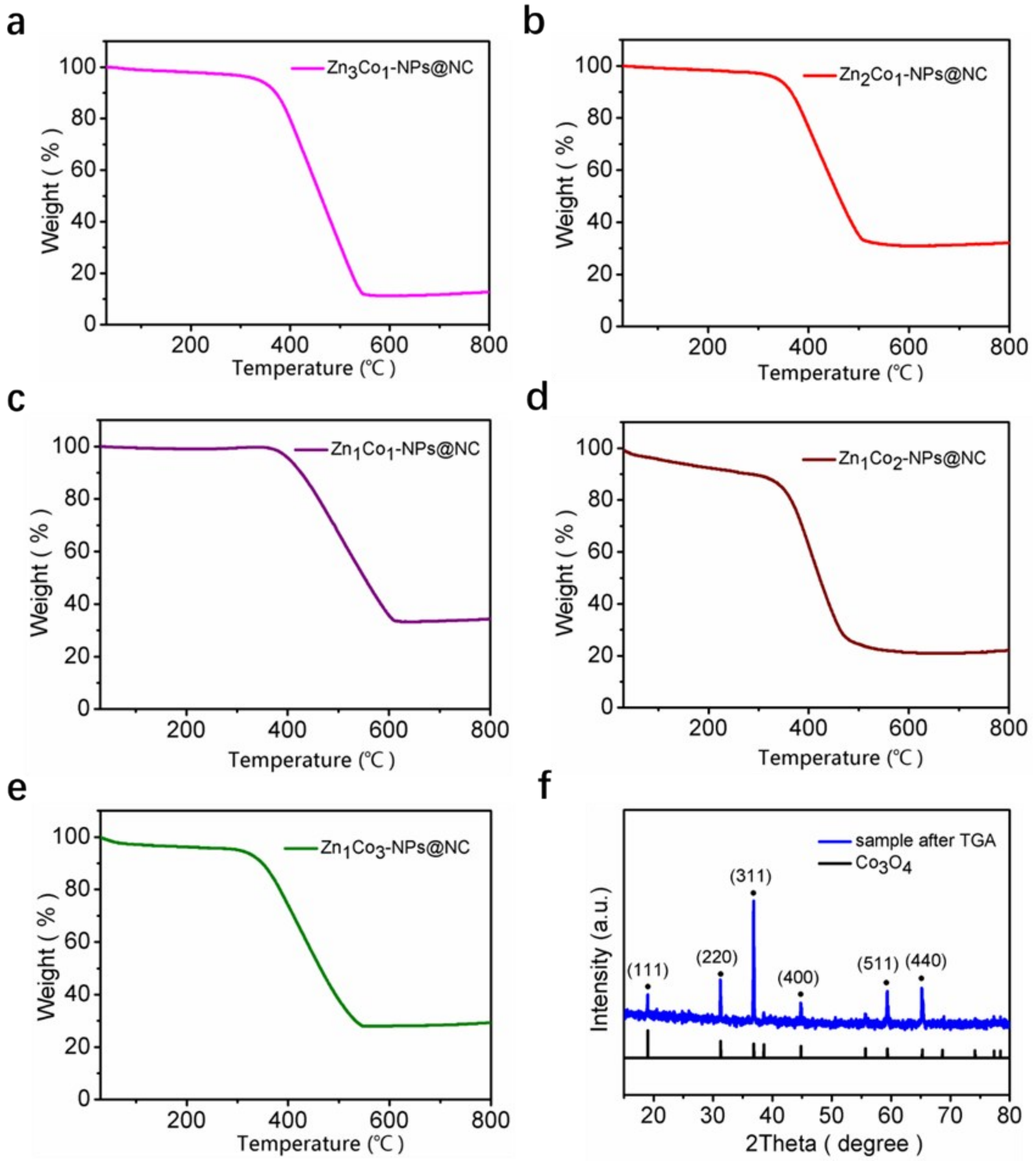

Fig. S7 (a-e) Thermogravimetric analysis of **Zn$_3$Co$_1$-NPs@NC**, **Zn$_2$Co$_1$-NPs@NC**, **Zn$_1$Co$_1$-NPs@NC**, **Zn$_1$Co$_2$-NPs@NC** and **Zn$_1$Co$_3$-NPs@NC.** (f)PXRD patterns of the simulated Co_3O_4 (black) and the samples after thermogravimetric analysis.

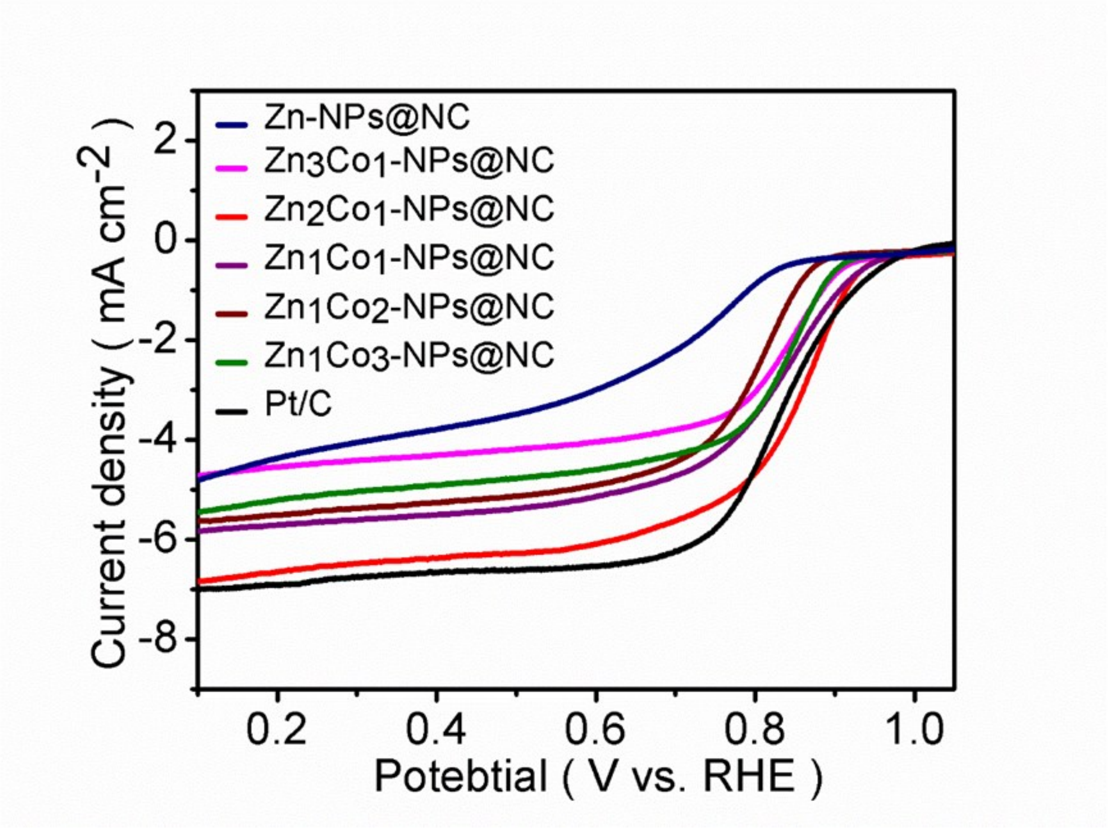

Fig. S8 Linear sweep voltammetry (LSV) curves at 1600 rpm of **Zn-NPs@NC**, **Zn_3Co_1-NPs@NC**, **Zn_2Co_1-NPs@NC, Zn_1Co_1-NPs@NC**, **Zn_1Co_2-NPs@NC** and **Zn_1Co_3-NPs@NC.**