Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Two-dimensional graphene-like N, Co-codoped carbon nanosheets derived from ZIF-67 polyhedrons for efficient oxygen reduction reaction

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Experimental Section

Chemicals

Cobaltous nitrate hexahydrate ($Co(NO_3)_2•6H_2O$, 99 %), 2-methylimizazolate (2-MI, $C_4H_6N_2$, 98 %), potassium chloride (KCl, 99.5 %) and lithium chloride (LiCl, 99.99 %) were purchased from Aladdin Reagent Co. Ltd (Shanghai, China). Ethanol and concentrated sulfuric acid were purchased from Tianjin Kermel Chemical Reagent Co. Ltd. (Tianjin, China). All chemicals were used without any treatment or purification.

The preparation of ZIF-67 nanoctystals

An ethanolic solution of cobaltous nitrate hexahydrate ($Co(NO_3)_2•6H_2O$, 0.05 mM) was added into an equal-volume ethanolic solution of 2-methylimizazolate (2-MI, 0.2 mM) with stirring. Then the entire reaction was performed without any disturbance at room temperature for 48 h. Subsequently, the resulting ZIF-67 precipitate was centrifuged and washed with ethanol for at least three times to insure the absolute removal of 2-MI ligands. The ZIF-67 nanoparticals were obtained by drying in an oven at 50 °C for 10 h.

Preparation of N, Co-CNSs and Co@NPCs

In a typical process, 100 mg ZIF-67 nanoparticles and 10 g eutectic salts (LiCl/KCl = 45/55 by weight) were mixed and homogenized with a ball mill for 2 h.

The powder mixture was transferred into a ceramic boat and placed in a temperature-programmed furnace under a continuous nitrogen flow. The powder mixture was heated to 800°C (or 600, 700 and 900°C) with a heating ramp of 5 °C/min from room temperature and kept for 1 h. The sample was obtained by washing with sulfuric acid solution (0.5 M) and deionized water, followed by freeze-drying for at least 48 h. The sample was labeled as N, Co-CNSs-T, where T referred to the pyrolysis temperature.

Co@NPCs was prepared by pyrolysizing ZIF-67 nanoparticles without salts but using the same pyrolysis procedure of N, Co-CNSs-800.

Characterization

The morphologies of the samples were observed using field emission scanning electron microscopy (FESEM, FEI Company, NOVA NanoSEM 450), transmission electron microscopy (TEM, FEI Tecnai G20, 200 KV) and and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai F30, 300 KV). The thickness of the carbon nanosheets was analyzed by Atomic force microscopy (AFM, MultiMode 3D). The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2400 diffractometer. The Raman analysis was carried out on RENISHAW inVia Raman Microscope with 633 nm excitation wavelength. X-rays photoelectron spectroscopy (XPS) measurements were conducted on Thermo ESCALAB250 with Al Kα X-rays radiation. Elemental analysis was performed on a vario EL III Elemental Analyzer (Elementar, Germany). The content of Co species was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima2000DV). The electrical conductivity of the samples was measured by a standard four-point probe resistivity measurement system Keithley 2000 (Keithley Instruments Inc., Cleveland, OH, USA).

Electrode preparation and electrochemical text

Electrode preparation. The electrocatalyst inks were prepared by ultrasonically dispersing catalyst (2.0 mg) in a mixed solution which consists of 200 μL deionized water, 780 μL ethanol and 20 μL 5 wt.% Nafion solution (Alfa Aesar). After ultrasound for 1 h, 10 μL of the ink was dropped onto a rotating disk electrode (RDE, 5 mm diameter, 0.196 cm^2 geometric surface areas) and rest at room temperature without any interruption for 1 h. The loading amount of the catalyst is 0.1 mg cm^{-2}.

Electrochemical text. Cyclic voltammetry (CV) and polarization curves data were recorded on an electrochemical workstation (CHI 760E, CHI Instrument, China) equipped with a three-electrode cell system. The whole test process was performed in the O_2-satured or Ar-satured 0.1 M KOH solution. All potentials in this study refer to reversible hydrogen electrode (RHE), E_{RHE} = E (Ag/AgCl) + 0.059× pH + 0.210. A Pt wire and an Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. CV spectra and polarization curves were collected at a scan rate of 10 mV s^{-1} and at 25 °C. All electrocatalytic measurements are carried out in a three-electrode cell using a rotating disk electrode (RDE, PINE Research Instrumentation) measurements at 25 °C.

The kinetic-limiting current density (J_K) for the ORR was derived from the experimental data using the Koutecky-Levich equation (Eq. 1):

$$\frac{1}{J}=\frac{1}{|J_L|}+\frac{1}{|J_K|}=\frac{1}{B\omega^{1/2}}+\frac{1}{|J_K|} \qquad (K-L)$$

$$B=0.62nFC_0(D_0)^{2/3}\upsilon^{-1/6}$$

$$J_K=nFkC_0$$

where J, J_K and J_L are the measured current density, kinetic- and diffusion-limiting current densities, respectively; *ω* is the angular velocity of the disk (ω = 2πN, N is the rotation speed), n is the electron transfer number, F is the Faraday constant (F = 96, 485 C mol^{-1}), C_0 is the bulk concentration of O_2 ($C_0 = 1.2 \times 10^{-6}$ mol cm^{-3} in 0.1 M KOH), D_0 is diffusion coefficient of O_2 ($D_0 = 1.9 \times 10^{-5}$ cm^2 s^{-1} in 0.1 M KOH), υ is the kinematic viscosity of the electrolyte (υ = 0.01 cm^2 s^{-1} in 0.1 M KOH), and k is the electron transfer rate constant. Commercial Pt/C (20 wt% Pt on carbon, Johnson Matthey) was used to compare the catalytic performance loading: 0.1 mg cm^{-2}).

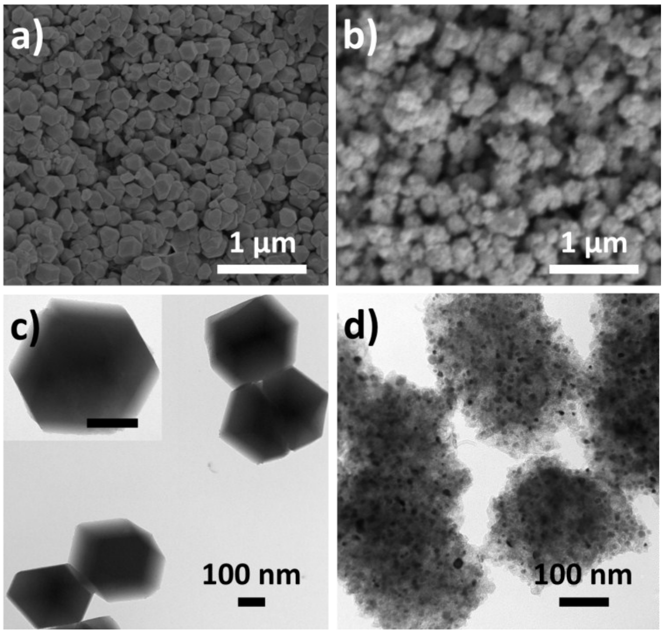

Fig. S1. FESEM (a) and TEM (c) images of ZIF-67, FESEM (b) and TEM (d) images of Co@NPCs

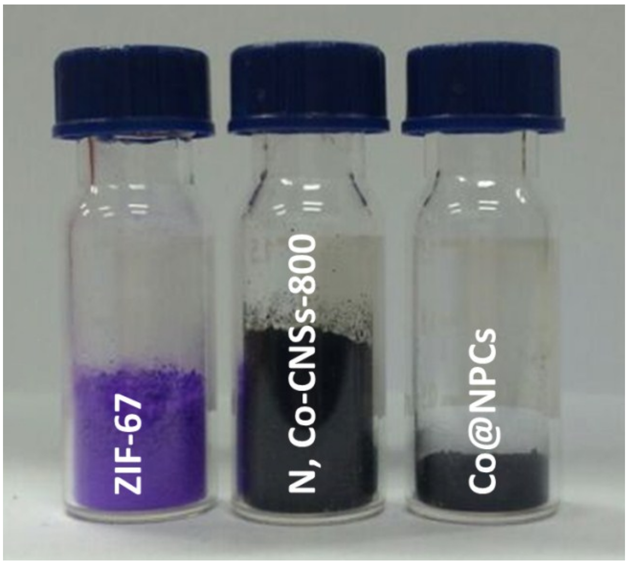

Fig. S2 A volume comparison of 100 mg powder ZIF-67 nanocrystals (left), N, Co-CNSs-800 (middle) and Co@NPCs (right).

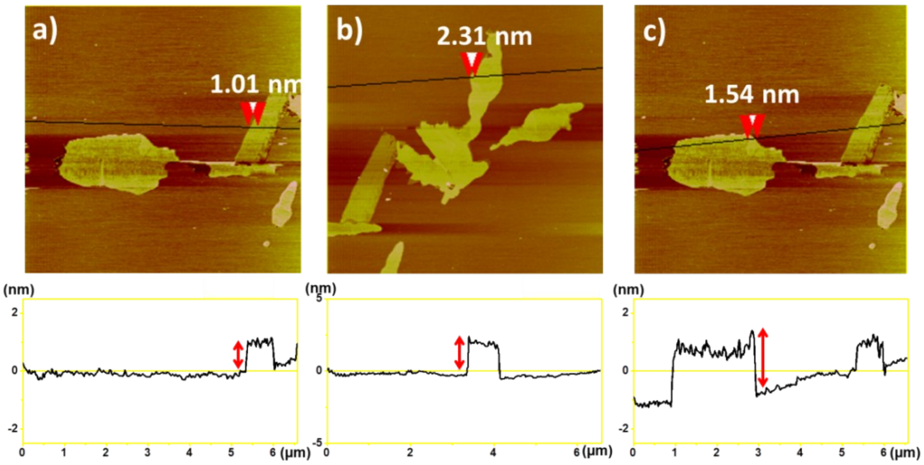

Fig. S3. The AFM images and responding heights of N, Co-CNSs-800.

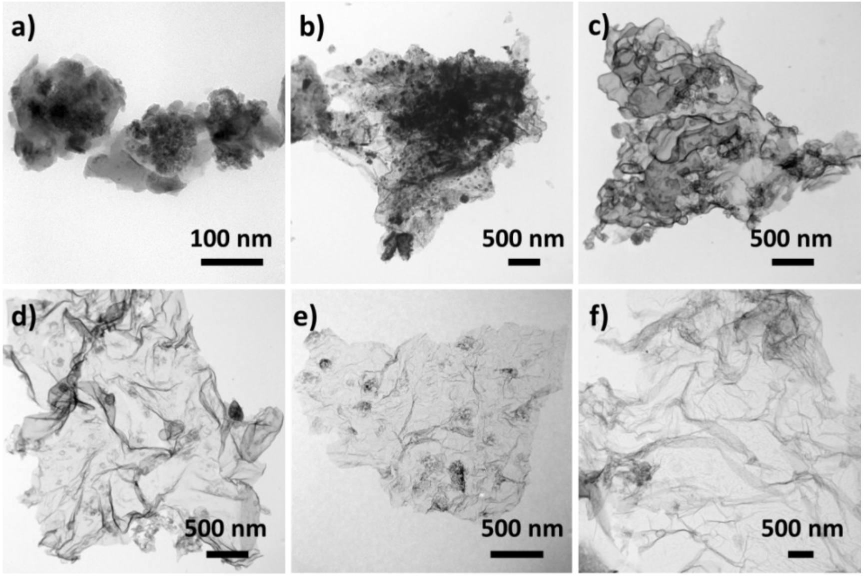

Fig. S4. TEM images of the samples obtained by pyrolyzing ZIF-67 in salts at different temperature for 1 h: (a) 450 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C and (f) 900 °C.

Table S1 Heteroatom content for Co@NPCs and N, Co-CNSs

Sample	N (wt %, by element analysis)	N (at %, by XPS)	Co (wt %, by ICP)
N, Co-CNSs-600	16.72	18.19	7.04
N, Co-CNSs-700	14.98	15.95	7.00
N, Co-CNSs-800	13.85	12.48	4.39
N, Co-CNSs-900	8.45	9.30	2.60
Co@NPCs	4.24	6.00	17.36

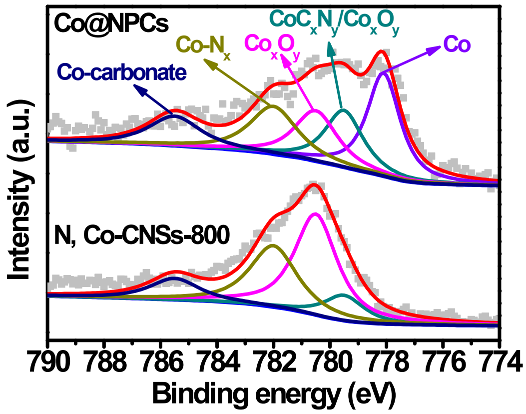

Fig. S5. High-resolution Co 2p spectra of Co@NPCs and N, Co-CNSs-800

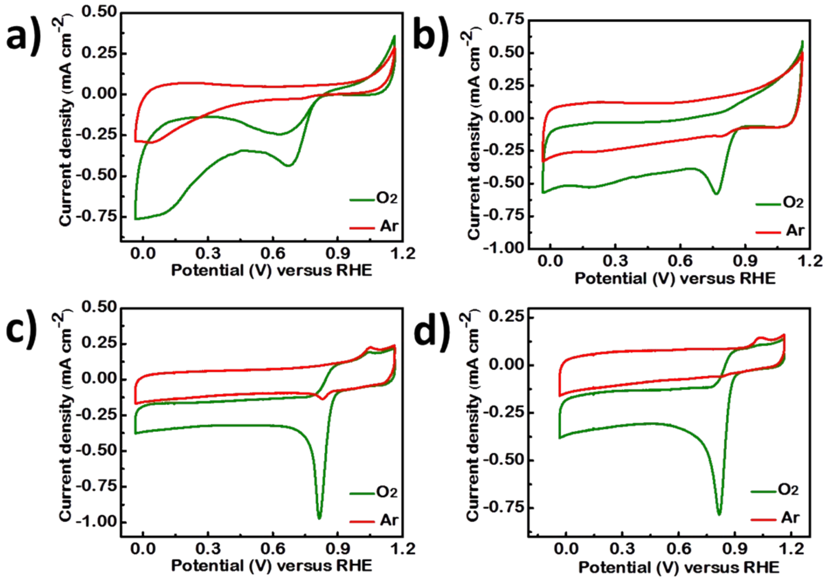

Fig. S6. CV curves of N, Co-CNSs-600 (a), N, Co-CNSs-700 (b), N, Co-CNSs-900 (c) and Co@NPCs (d) in Ar and O_2 saturated 0.1 M KOH solution at a scan rate of 10 mV s^{-1}.

Table S2 Comparison of ORR catalytic performances between N, Co-CNSs and Co@NPCs

Sample	Cathodic peak (V)	Set-on potential (V)	Half-wave potential (V)	Limited current density (mA cm^{-2})
Co@NPCs	0.81	0.93	0.80	-3.8
N, Co-CNSs-600	0.47	0.88	0.74	-3.8
N, Co-CNSs-700	0.61	0.95	0.81	-4.4
N, Co-CNSs-800	0.84	0.96	0.83	-4.7
N, Co-CNSs-900	0.81	0.93	0.81	-4.3

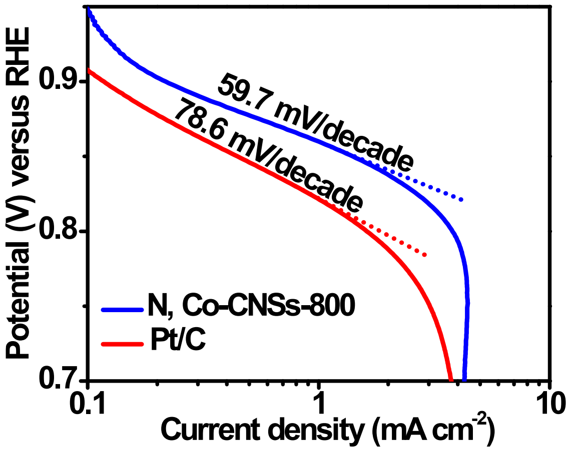

Fig. S7. Tafel slopes curves of N, Co-CNSs-800 and Co@NPCs derived from Fig. 3b.

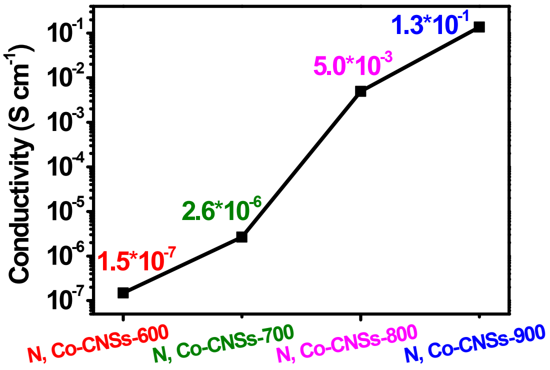

Fig. S8. The conductivity of N, Co-CNSs-T.

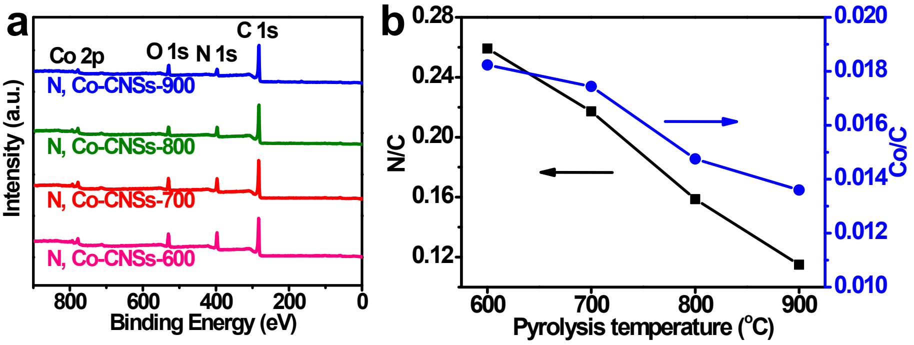

Fig. S9. (a) XPS survey of N, Co-CNSs-600, N, Co-CNSs-700, N, Co-CNSs-800 and N, Co-CNSs-900, (b) the atomic ratio between nitrogen and carbon (N/C) and the atomic ratio between cobalt and carbon (Co/C) of N, Co-CNSs-600, N, Co-CNSs-700, N, Co-CNSs-800 and N, Co-CNSs-900.

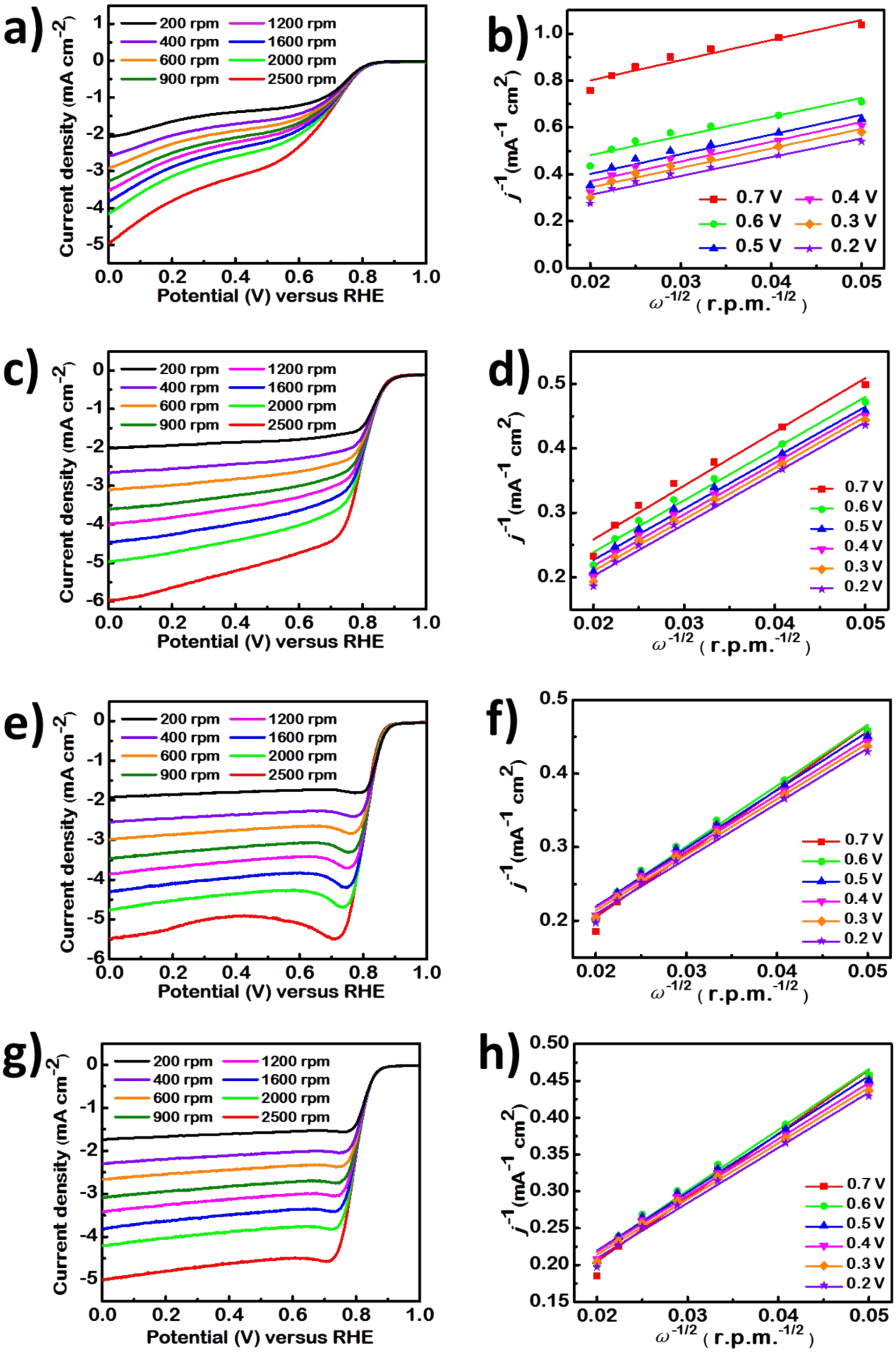

Fig. S10 LSV curves at various rotating speeds and corresponding K–L plots at various potentials from 0.2 V to 0.7 V: (a, b) N, Co-CNSs-600, (c, d) N, Co-CNSs-700, (e, f) N, Co-CNSs-900, (g, h) Co@NPCs.