Facile synthesis of three-dimensional Co/N co-doped carbon nanocuboid for enhanced oxygen reduction reaction

Xinyu Zhang,[a,1] Wenkai Huang[a,1] Jun Zhang,[a,c]* Yanlan Wang,[a,b] Didier Astruc[d]* and Xiang Liu[a]*

[a]Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, College of Materials and Chemical Engineering, China Three Gorges University, Yichang, Hubei 443002, China. E-mail: xiang.liu@ctgu.edu.cn

[b]Department of chemistry and chemical engineering, Liaocheng University, 252059 Liaocheng, China

[c]College of Metallurgy and Materials Engineering, Chongqing Key Laboratory of Nano/Micro Composites and Devices, Chongqing University of Science and Technology, Chongqing 401331, China. E-mail: junzhang@cqust.edu.cn

[d]ISM, UMR CNRS N° 5255, Université de Bordeaux, 351 Cours de la Libération, 33405 Talence Cedex, France. E-mail: didier.astruc@u-bordeaux.fr

[1]These authors have equally contributed to this work and should be considered as co-first authors

Table of Contents

1. Chemicals and reagents

All chemicals and solvents were used without further purification. Platinum on carbon (Pt/C, 20 wt%) and nafion (5%) was supplied from Shanghai hesen Co., Ltd. Benzimidazole($C_7H_6N_2$) was purchased from Macklin Reagent Co., Ltd. Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 99.99%) was purchased from Shanghai Jiuding Chemical Technology Co., Ltd. Dicyandiamide was obtained from Aladdin Regent Co., Ltd., MeOH was supplied from Wuhan Xinshenshi Chemical Technology Co., Ltd. Triethylamine (NEt_3) was purchased from Macklin Reagent Co., Ltd.

2. Characterization

Morphology analysis by transmission electron microscopy (TEM) measurements were performed on a JEOL 2100F (Japan) at an accelerating voltage of 200 kV. Surface analysis by XPS was performed with a Thermo SCIENTIFIC ESCALAB 250Xi (ThermoFischer, USA) system spectrometer in an ultra-high vacuum (UHV) chamber. XRPD was performed on a BRUKER D8 ADVANCE. The morphologies of the catalysts were observed by scanning electron microscopy (SEM, FEI NOVA NANO450). Raman spectra the of catalysts were measured on a Renishaw inVia(10.16.0.143). The textural properties of catalysts were tested by N_2 sorption isotherms on a ASAP-2460.

3. Preparation of ZIF-9

First, 1.18 g of benzimidazole was dissolved into 150 mL of methanol, and 1.4 g of cobalt nitrate hexahydrate was dissolved into 250 mL of methanol. Then, the above two solutions were mixed into a flask. Next, triethylamine (300 μL) was added into the above solution, and the resulting mixture was stirred continuously at 30 °C for 8 h. The precipitated solid was separated and washed 3 times with methanol, then dried in a vacuum oven at 50 °C for overnight.

4. Preparation of g-C₃N₄

In brief, dicyandiamide was heated to 550°C, with a rate of 5°C/min, for 2 h. As a result, g-C_3N_4 nanosheets were obtained.

5. Preparation of CoN/CNCs-800

150 mg of g-C$_3$N$_4$ and 50 mg of ZIF-9 were added into 10 mL of methanol solution, and this mixture was stirred for 6 h at room temperature. The precipitated solid was separated and washed with 3 times methanol, then dried in a vacuum oven at 80 °C for overnight. The precipitated solid was sintered at 800 °C, with the heating rate of 5 °C/min, under nitrogen atmosphere for 2 h to obtain CoN/CNCs-800.

6. Electrocatalytic Measurements

The oxygen reduction properties were measured in a three-electrode beaker cell using a CHI 660E electrochemical workstation in 0.1 M KOH solution. The working electrode is glassy. Here, a platinum wire was used as counter electrode, and Ag/AgCl calibrated with respect to reversible hydrogen electrode (RHE) was used as the reference electrode. The catalyst ink was prepared by ultrasonically dispersing 5 mg of catalyst in a mixture of 480 μL water, 480 μL absolute ethanol and 40 μL of 5 wt% Nafion solution. First, the surface of the glassy carbon electrode was polished to a bright state followed by dropping the catalyst ink (10 μL) onto the glassy carbon disk electrode (5 mm diameter) and then drying at room temperature. The cyclic voltammetry curves were recorded at a scan rate of 50 mV s^{-1} in an O$_2$ (N$_2$)-saturated 0.1 M KOH electrolyte. Before the ORR measurements, repeated cyclic voltammetry pretreatment of the samples was conducted for up to 20 cycles until obtaining a stable curve. The linear scan voltammetry curves were recorded at a scan rate of 10 mV s^{-1} for each sample (rotation speed: 800-2500 rpm, scan range: 0.05-1.2 V *vs* RHE). The suspension was dried in air with a mass loading of 0.22 mg cm^{-2}.

All the potentials measured above were converted to the reversible hydrogen electrode (RHE) according to the following Nernst equation: $E_{RHE} = E_{Ag/AgCl} + (0.198 + 0.059 \times pH)$. The electron-transfer number (n) and kinetic current density (J_k) were calculated from the Koutecky-Levich (K-L) equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{0.62nFC_oD_o^{\frac{2}{3}}V^{-\frac{1}{6}}\omega^{\frac{1}{2}}} + \frac{1}{J_K}$$

where J is the measured current density, J_L is the diffusion-limiting a current density, F is the Faraday constant (96485 C mol^{-1}); C_0 is the O$_2$-saturated concentration in 0.1 M KOH solution; D_0 is the O$_2$ diffusion coefficient; V is the kinetic viscosity of solution, and ω is the rotation rate of the electrode. J_k was calculated at half-wave potential with a rotating speed of 1600 rpm.

7. Electrochemical properties and characterizations of CoN/CNCs (Fig S1-S4)
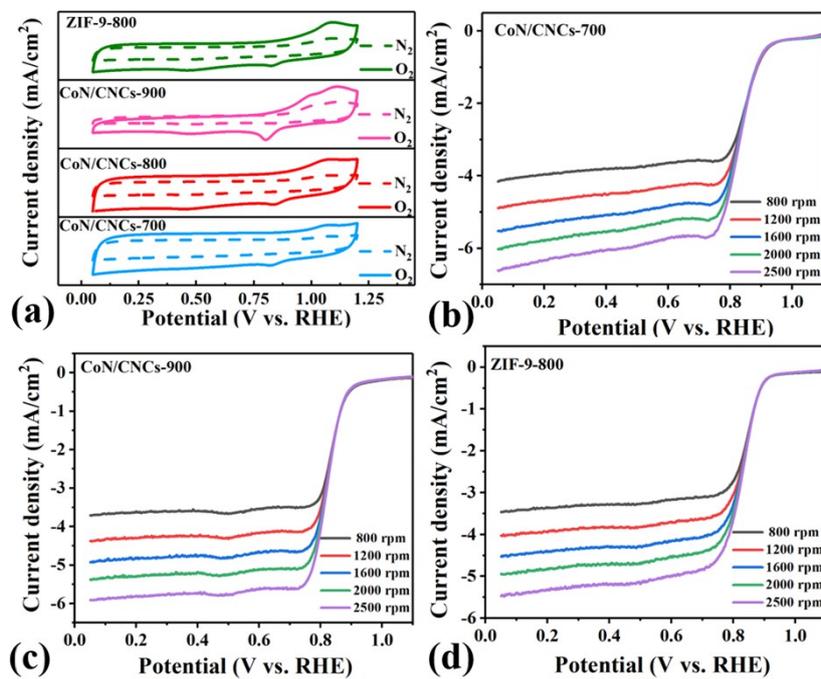
Figure S1. (a) CV curves of CoN/CNCs, ZIF-9-800 recorded in N_2- and O_2-saturated 0.1 M KOH solution; (b) LSV curves of CoN/CNCs-700 tested under various rotation speeds; (c) LSV curves of CoN/CNCs-900 tested under various rotation speeds; (d) LSV curves of ZIF-9-800 tested under various rotation speeds.
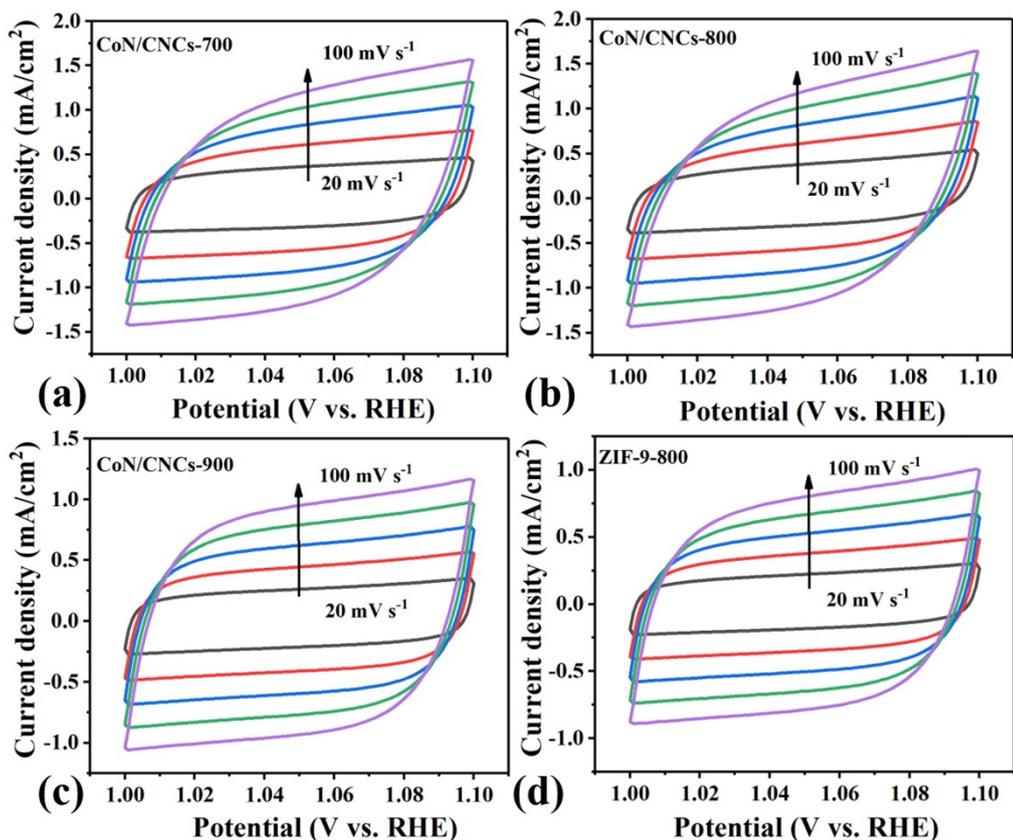
Figure S2. CV curves of (a) CoN/CNCs-700, (b) CoN/CNCs-800, (c) CoN/CNCs-900, (d) ZIF-9-800.
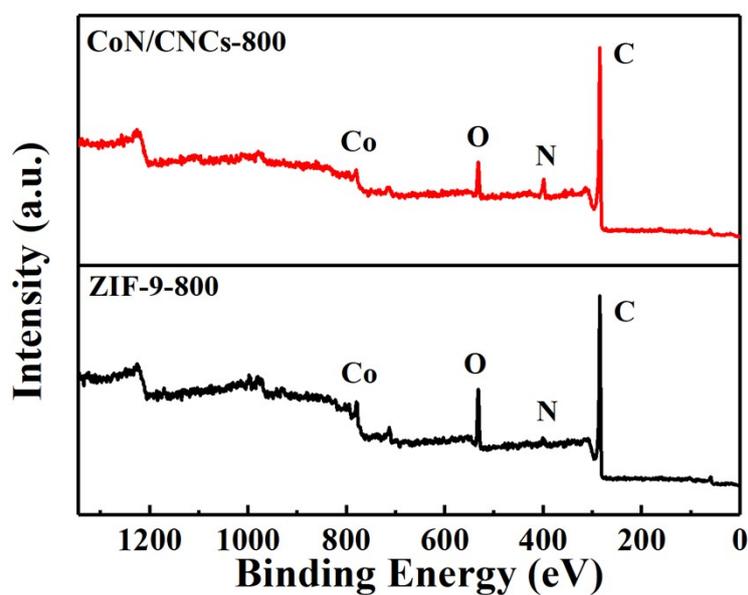
Figure S3. XPS survey spectrums
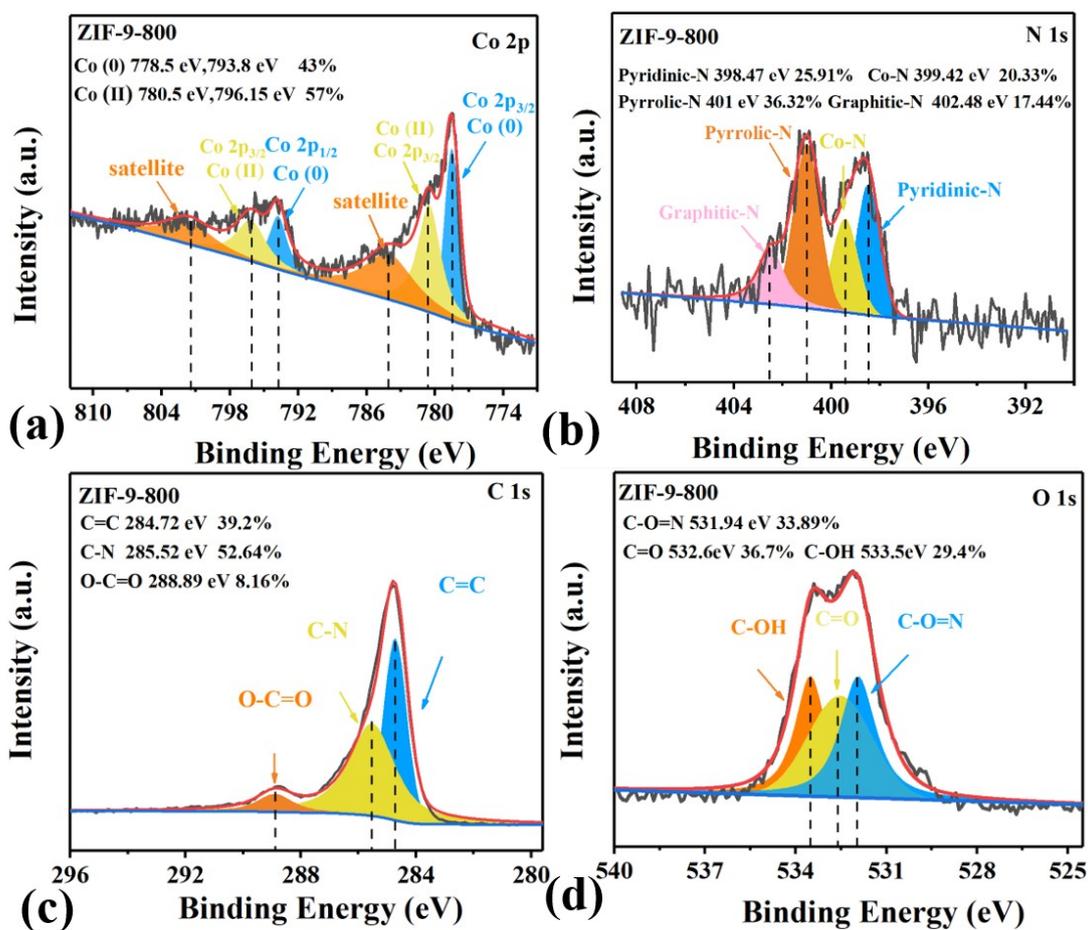
Figure S4. (a) Co 2p, (b) N 1s, (c) C 1s and (d) O 1s XPS of ZIF-9-800.

Table S1: The content of atoms for ZIF-9-800 and CoN/CNCS-800

Examples	Co	N	C	O
CoN/CNCS-800	1.74%	8.26%	81.72%	8.28%
ZIF-9-800	2.12%	3.86%	81.42%	12.6%