

## Supporting Information

### **NaCl Protected Synthesis of 3D Hierarchical Metal-free Nitrogen-doped Carbon Catalysts for Oxygen Reduction Reaction in Acidic Electrolyte**

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## 1. Experimental

Before the synthesis of NC-1:1:10, the NaCl salt was conducted to grinding for 2 h.

For the synthesis of NC-1:1:10, 0.5 g polyacrylonitrile (PAN) was firstly dissolve in N,N-Dimethylformamide (DMF, 5 mL) with continuous stirring at 60 °C. Then, 0.5g zinc oxide (ZnO) nanoparticles dissolved in DMF (3 mL) was dropwise added into the PAN solutions with 12 h vigorous stirring. After that, the resulting mixture was grinded with 5g NaCl salt for 2h. The collected composites were the transferred into a muffle furnace and heated at 220°C for 2 h with a heating rate of 2°C/min. The sample was cooled to room temperature, and then heated to 900°C at a heating rate of 5°C/min and held at 900°C for 2 h under flowing N<sub>2</sub>. The obtained black powder was washed with 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at 80°C for 8 h followed by centrifugation, washing and freeze-drying.

Synthesis of NC-1:0:0, NC-1:0:10 and NC-1:1:0. The contrast sample was prepared under conditions similar to that used for NC-1:1:10. For NC-1:0:0, ZnO and NaCl was not used. For NC-1:0:10, ZnO was not used. For NC-1:1:0, NaCl was not used.

## 2. Electrochemical measurements

All electrochemical experiments were performed in a standard three-electrode cell at room temperature. The cell consisted of a glassy carbon working electrode (GC electrode, 5 mm in diameter, PINE: AFE3T050GC), an Ag/AgCl (saturated KCl) reference electrode, and a carbon rod counter electrode. All potentials in this study, however, are given relative to a reversible hydrogen electrode (RHE). The working electrodes were prepared by applying catalyst ink onto glassy carbon (GC) disk electrodes. In brief, the electrocatalyst was dispersed in ethanol and ultrasonicated for 30 minutes to form a uniform catalyst ink (10 µg µL<sup>-1</sup>). A total of 10 µL of catalyst ink was then pipetted on the glassy carbon surface, leading to a loading of 0.5 mg cm<sup>-2</sup>.

After drying at room temperature, a drop of 0.01wt% Nafion solution (Dupont) was applied onto the surface of the catalyst layer to form a thin protective film. The prepared electrodes were dried at room temperature before the electrochemical tests. All of the electrodes were pretreated by cycling the potential between 0 and 1.2 V at a sweep rate of 50 mV s<sup>-1</sup> for 50 cycles in order to remove any surface contamination prior to ORR activity testing.

The activities of catalysts were performed by recording linear sweep voltammetry (LSV) curves in the oxygen-saturated 0.1 M HClO<sub>4</sub> solution. The LSV curves for ORR were recorded at potential scan rate of 10 mV s<sup>-1</sup>. The rotation speed was controlled at 1,600 rpm.

Rotating disk electrode (RDE) measurements were conducted at rotation speeds from 100 to 2,500 rpm using a VersaSTAT3 (V<sub>3</sub>). RDE measurements were conducted in O<sub>2</sub>-saturated 0.1 M KOH solution at 10 mV s<sup>-1</sup> scan rate. The electron transfer number (*n*) was analyzed on the basis of Koutecky-Levich equations:

$$\frac{1}{J} = \frac{1}{J_D} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (1)$$

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

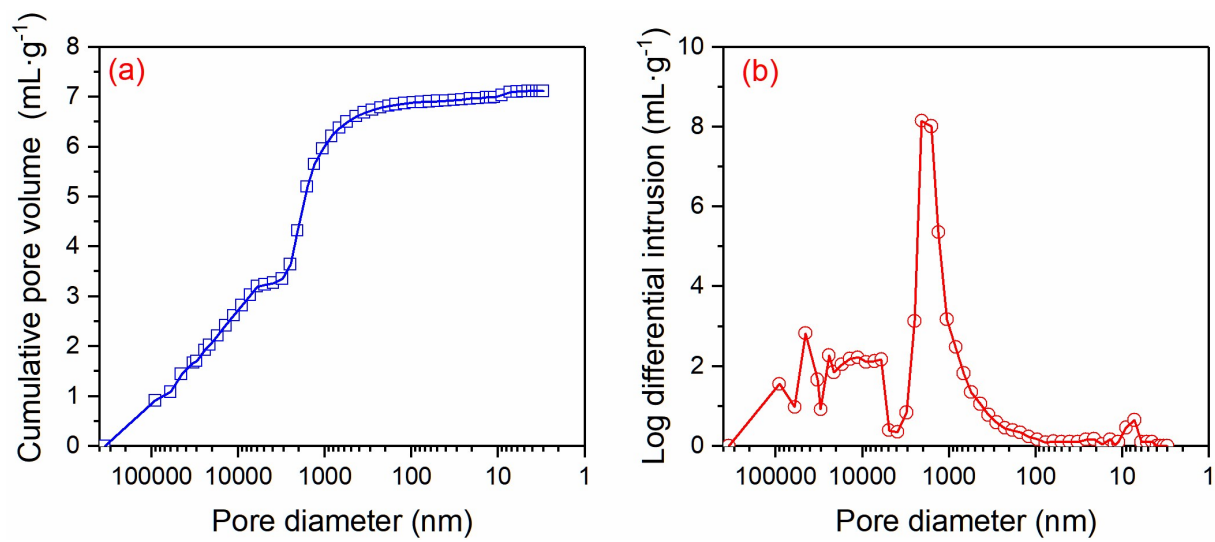
in which *J* is the measured current density, *J<sub>K</sub>* and *J<sub>D</sub>* are the kinetic- and diffusion-limiting current densities,  $\omega$  is the angular velocity of the disk ( $\omega = 2\pi N$ , *N* is the linear rotation speed), *n* is the overall number of electrons transferred in ORR, *F* is the Faraday constant (*F*=96,485 C mol<sup>-1</sup>), *C<sub>0</sub>* is the bulk concentration of O<sub>2</sub>, *v* is the kinematic viscosity of the electrolyte, and *k* is the electron transfer rate constant. According to Equations (1) and (2), the number of electrons transferred (*n*) and *J<sub>K</sub>* can be obtained from the slope and intercept of the Koutecky–Levich plots, respectively. By using the value *C<sub>0</sub>*=1.2×10<sup>-3</sup> mol L<sup>-1</sup>, *D<sub>0</sub>*=1.93×10<sup>-5</sup> cm s<sup>-1</sup> and *v*=0.01 cm<sup>2</sup> s<sup>-1</sup> in 0.1M HClO<sub>4</sub>

### 3. Characterization

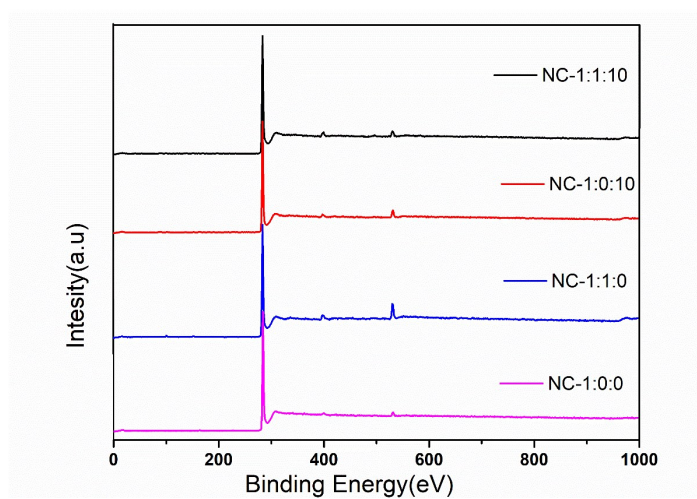
*SEM test:* Scanning electron microscope (SEM) was obtained using a JSM-7800F (JEOL) field emission scanning electron microscope operated at an acceleration voltage of 15 kV.

*Raman spectrum test:* Raman spectrum was recorded by a LabRamHR evolution Raman spectrometer equipped with a Nb-Yag laser excitation source operated at 532 nm.

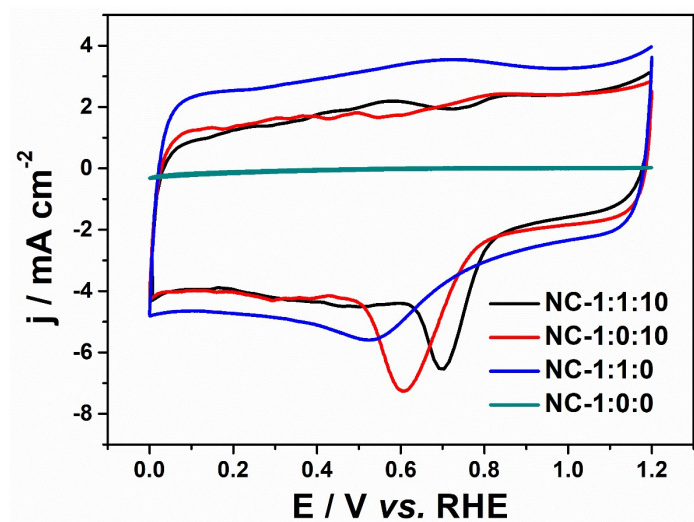
*XPS test:* X-ray Photoelectron Spectroscopy (XPS) was conducted on a PE PHI-5400 spectrometer equipped with a monochromatic Al X-ray source (Al KR, 1.4866 keV).



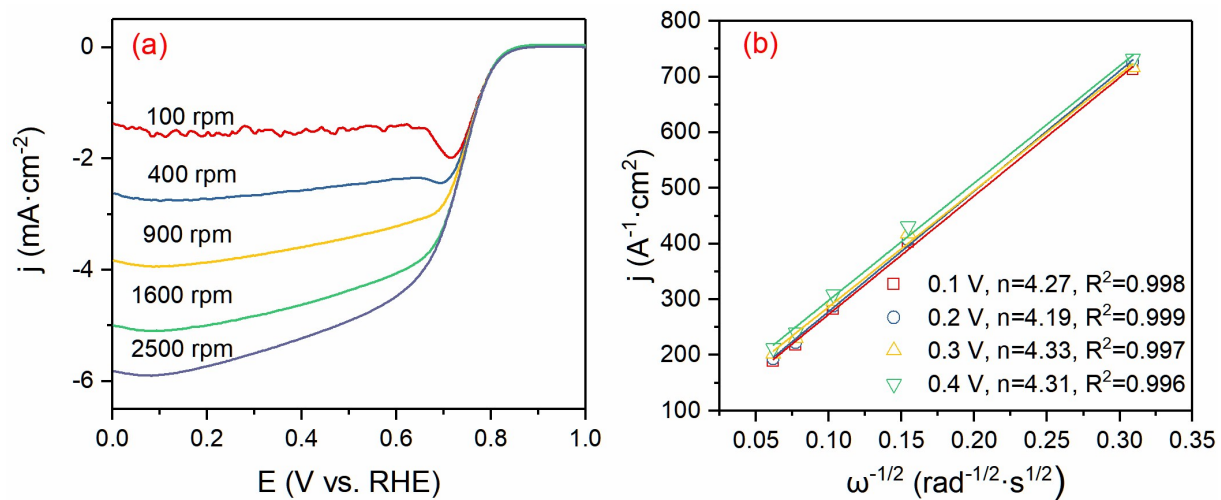
**Fig. S1** Pore distribution of NC-1:1:10 obtained from Hg intrusion.



**Fig. S2** XPS survey spectrum of catalysts.



**Fig. S3** CVs of catalysts in  $O_2$ -saturated 0.1 M  $HClO_4$  solution at a sweep rate of  $50 \text{ mV s}^{-1}$ .



**Fig. S4** LSVs (a) and K-L plots (b) at different rotating speeds of NC-1:1:10



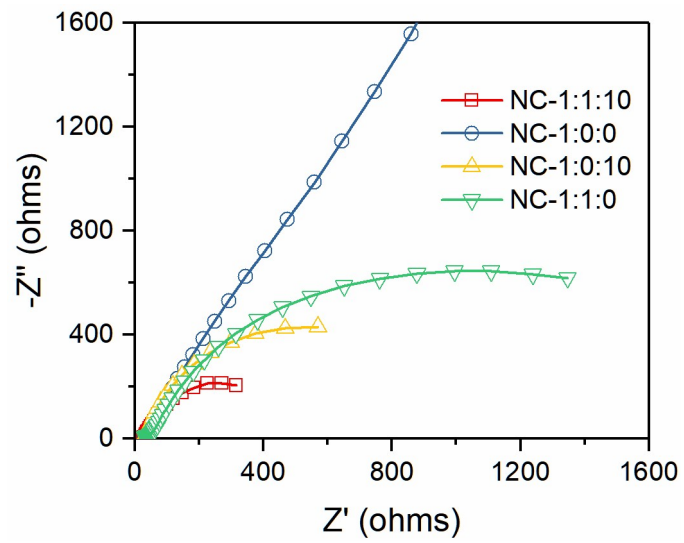


Fig. S5 Nyquist plot obtained by potentiostatic electrochemical impedance spectroscopy at 0.5V.

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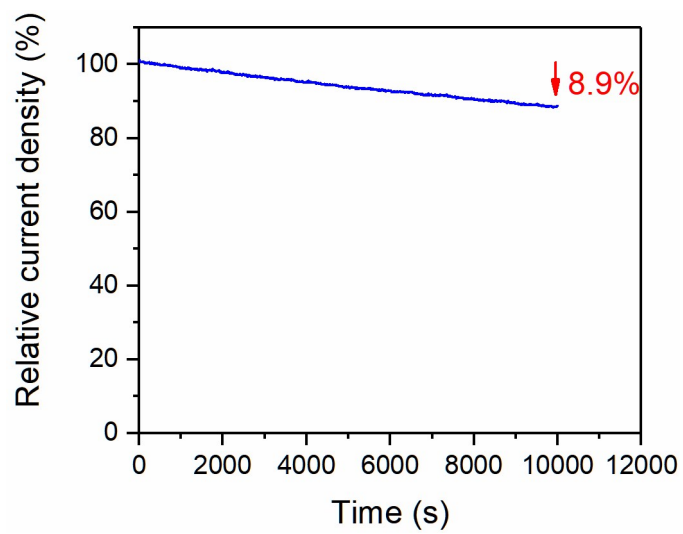


Fig. S6 Normalized chronoamperometry curves for NC-1:1:10

**Table S1** Specific area, pore volume, and element information of different catalysts.

Sample	Specific area (m <sup>2</sup> ·g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> ·g <sup>-1</sup> )	N (%)	Pyridinic N (%)	Pyrrolic N (%)	Quaternary N (%)	Oxidized N (%)
NC- 1:1:10	888.15	2.21	4.7	44.4	4.5	40.4	10.7
NC- 1:0:10	558.82	0.67	3.6	27.9	9.9	49.8	12.4
NC- 1:1:0	1044.47	1.10	2.6	36.5	23.7	20.8	19.0
NC- 1:0:0	181.33	0.14	1.6	33.2	32.0	16.9	17.9