

*Supporting information*

**S/N Codoped Carbon Nanotubes as an Efficient ORR  
Electrocatalyst for Zinc-Air Batteries**

Hong-Cheng Li, Peng-Cheng Ji, Yang Teng, Hai-Lang Jia,\* Ming-Yun Guan

School of Chemistry and Chemical Engineering, Institute of Advanced Functional Materials for Energy, Analysis and Testing Center of Jiangsu University of Technology, Jiangsu University of Technology, Changzhou 213001, P. R. China.

## Electrochemical measurements

A conventional three-electrode system was employed to evaluate the electrocatalytic performance of the obtained catalyst on a CHI 760E electrochemical workstation. A rotating disk electrode (RDE) with a glassy carbon (GC) disk (electrode area: 0.1256 cm<sup>2</sup>) was used as the working electrode, Ag/AgCl was used as the reference electrode, and platinum wire was used as the counter electrode. The rotating ring disk electrode measurements for ORR were carried out on RRDE in a N<sub>2</sub> or O<sub>2</sub>-saturated 0.1 M KOH electrolyte solution at a scan rate of 10 mV/s at various rotation rate of 1600rpm. Linear sweep voltammetry (LSV) at a scan rate of 10 mV/s was conducted in 0.1 M KOH at room temperature. Before the electrochemical measurements, the electrolyte solution was purged with O<sub>2</sub> for 30 min to achieve an O<sub>2</sub>-saturated solution, and stable polarization curves were recorded after 20 cycles. All the potentials were converted to the potential versus the reversible hydrogen electrode (RHE) according to  $E_{vsRHE} = E_{vsAg/AgCl} + E_oAg/AgCl + 0.059 \text{ pH}$ .

The RDE measurements were performed at different rotating speeds from 400 to 1600 rpm at a scan rate of 10 mV s<sup>-1</sup>. Koutecky-Levich plots were used to investigate the effective electron-transfer number and the mass-transport corrected current density for ORR at different potentials. According to the Koutecky-Levich equation:

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

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

$$J_k = nFkC_0 \quad (3)$$

Where  $\omega$  is the angular velocity,  $J$  is the measured current density,  $J_K$  and  $J_L$  are the kinetic and diffusion-limiting current densities.  $F$  is Faraday constant (96485 C mol<sup>-1</sup>),  $D_0$  is the diffusion coefficient of O<sub>2</sub> (1.9×10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>),  $\nu$  is the kinetic viscosity of the electrolyte (0.01 cm<sup>2</sup> s<sup>-1</sup>) and  $C_0$  is the bulk concentration of O<sub>2</sub> (1.2×10<sup>-6</sup> mol cm<sup>-3</sup>),  $n$  is the electron transfer number.  $B$  can be determined from the slope of the K-

L plots, and then the electron transfer number  $n$  can be obtained.

Rotating ring-disk electrode (RRDE) measurements were recorded with catalyst inks and electrodes prepared by the same method as that for the RDE measurements. The  $\text{H}_2\text{O}_2$  produced and the electron number ( $n$ ) transferred during the ORR were calculated using the following equations:

$$n = 4 \frac{I_D}{I_D + I_R/N}$$

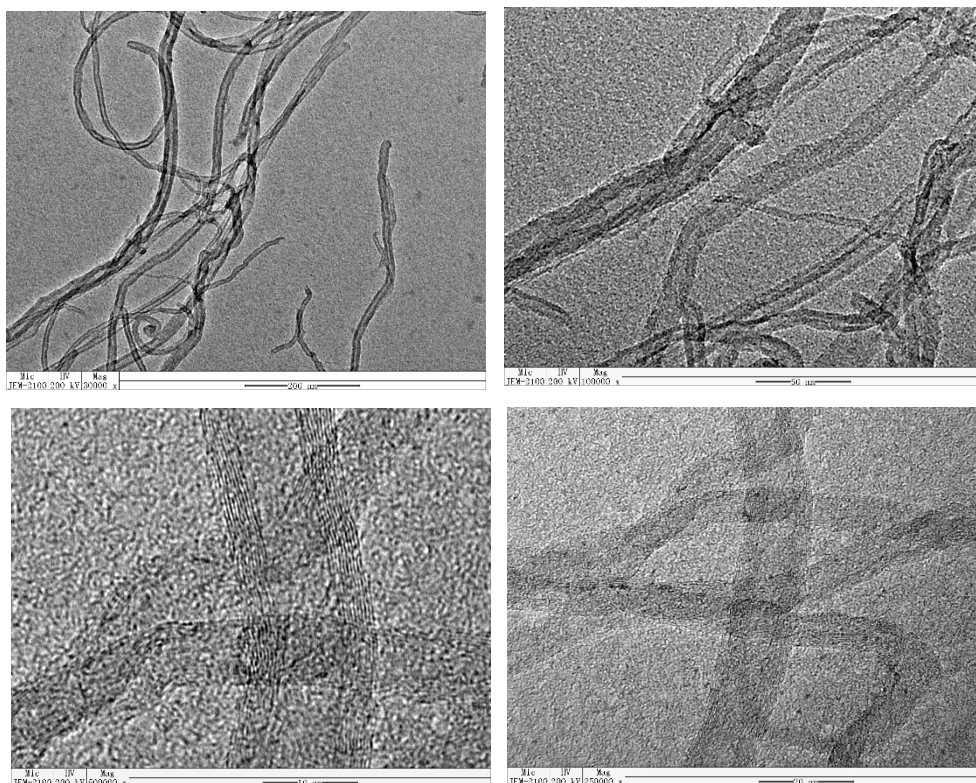
$$\text{H}_2\text{O}_2\% = 100 \times \frac{4 - n}{2}$$

The rotating ring-disk electrode was employed to detect the  $\text{H}_2\text{O}_2$  yield, where the ring potential was set to 1.3 V (vs. RHE). where  $I_D$  is the Faradaic current at the disk,  $I_R$  is the Faradaic current at the ring, and  $N= 0.37$  is the collection efficiency of ring electrode.

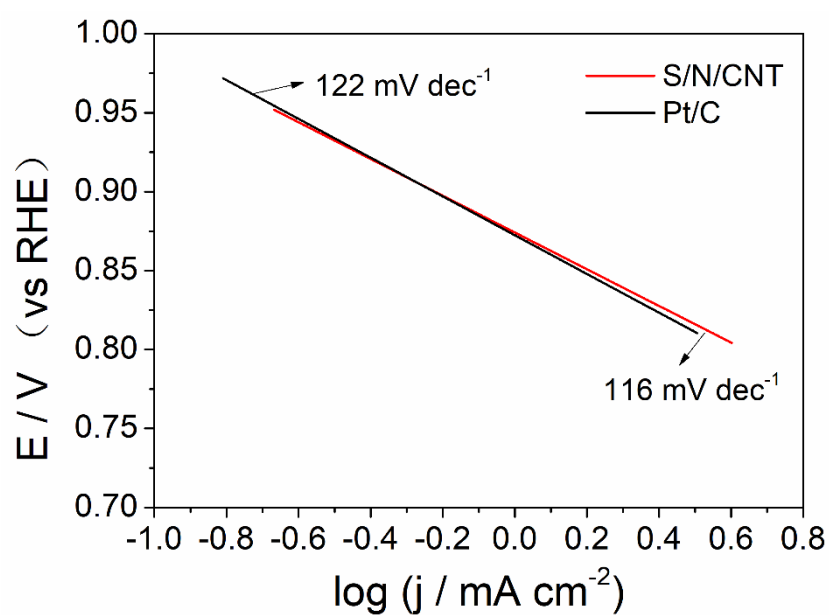
The electrochemical impedance spectroscopy (EIS) measurements were performed in the  $\text{O}_2$ -saturated 0.1 M KOH solution in the frequency range of  $10^6$  Hz to  $10^{-1}$  Hz at 0.85 V vs. RHE with 10 mV amplitude. Electrochemically active surface areas (ECSAs) were calculated according to the measured double-layer capacitance (Cdl) of samples on GC electrode with RDE by CV curves at different scan rates of 20-120  $\text{mV s}^{-1}$  in the non-Faradaic potential region (1.04-1.16 V vs RHE). A straight line can be obtained by plotting the current density against the scan rate at a specific potential in the CV curves. The slope of the straight line is defined as electrochemical double-layer capacitance (Cdl).

The measurements of the zinc–air batteries were performed using home-built electrochemical cells. The electrolyte was 6.0 M KOH/0.2 M zinc acetate. Zinc foil was used as the anode and the catalyst of S/N/CNT or Pt/C sprayed onto the foamed nickel ( $1 \text{ cm} \times 1 \text{ cm}$ ) with a loading of  $1.5 \text{ mg cm}^{-2}$  was used as the air-cathode, respectively. Cell guard 3501 membrane was used for a separator. The GDL had an effective area of  $1 \text{ cm}^2$  and allows  $\text{O}_2$  from ambient air to reach the catalyst sites. Measurements were carried out on the as-fabricated cell with a CHI 760E

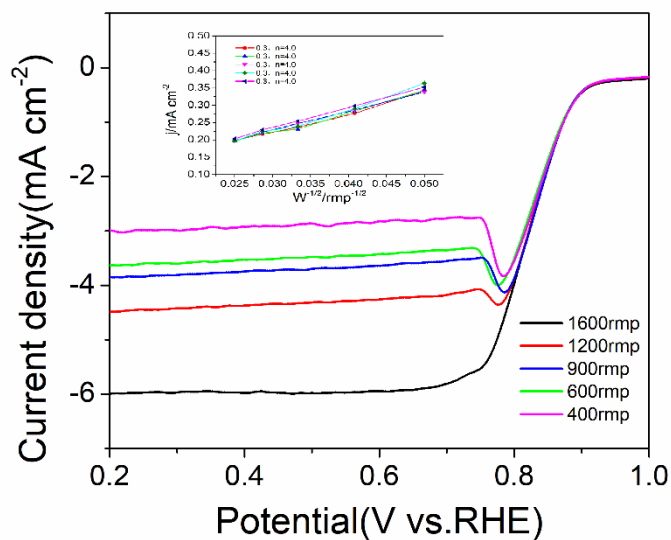
electrochemical workstation and a LAND CT2001A multichannel battery testing system at room temperature.



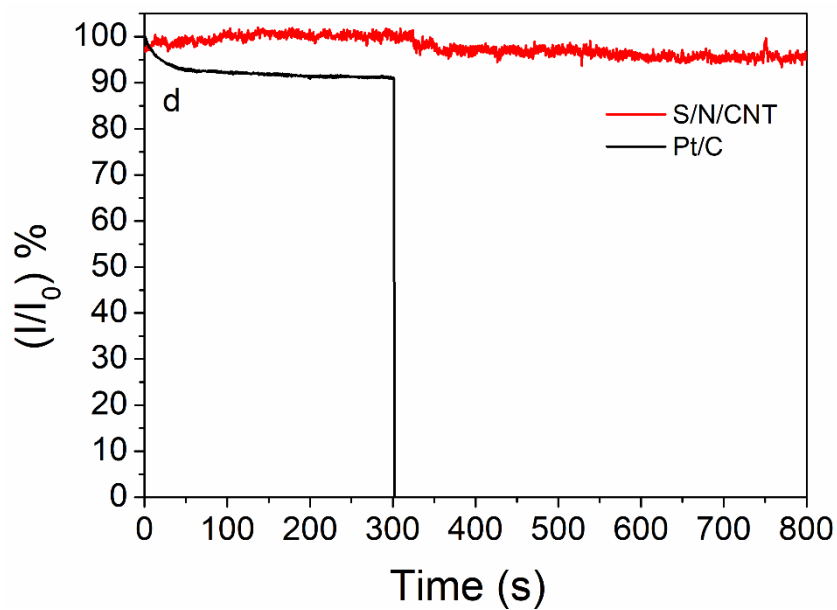
**Fig. S1** TEM of S/N/CNT



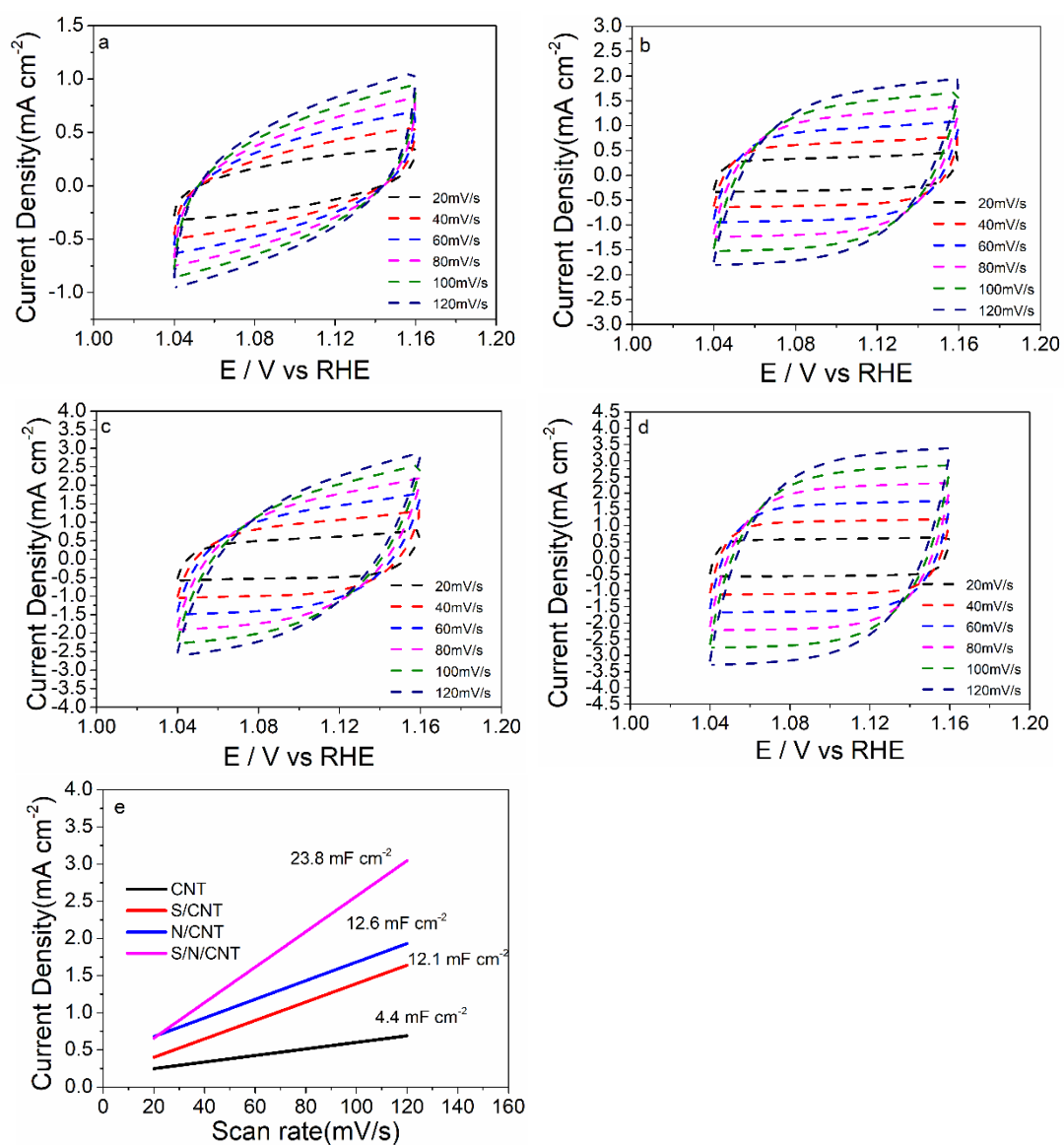
**Fig. S2** Tafel plots of S/N/CNT and Pt/C.



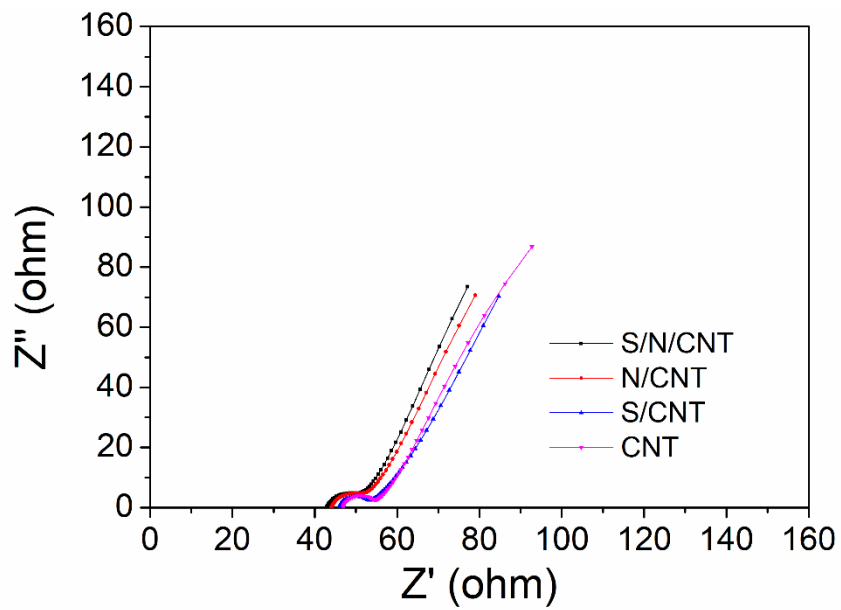
**Fig. S3** LSV of S/N/CNT in  $\text{O}_2$ -saturated 0.1 M KOH solution at different rotation rates, the illustration is corresponding K-L plots.



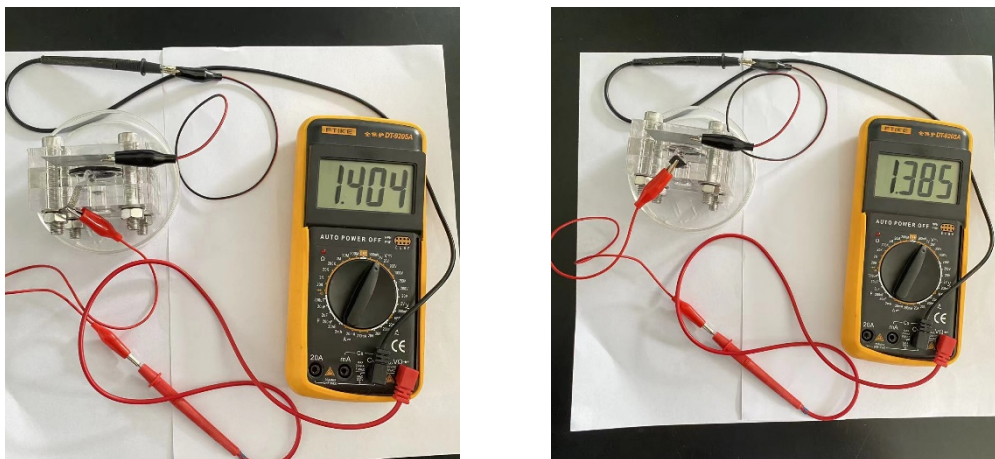
**Fig. S4** Methanol tolerance tests for S/N/CNT and commercial Pt/C in 0.1 M KOH with the addition of 3 M methanol.



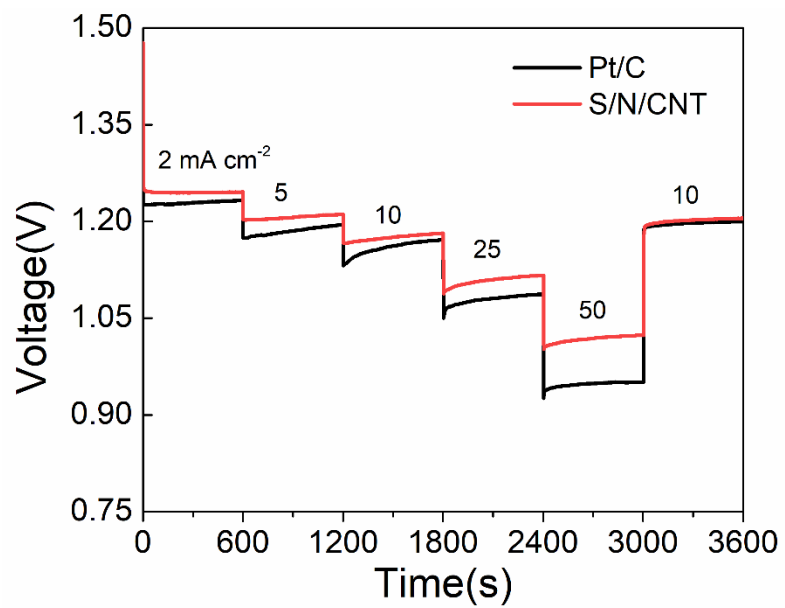
**Fig. S5** (a) CV curves of CNT in 0.1 M KOH, (b) CV curves of S/CNT in 0.1 M KOH, (c) CV curves of N/CNT in 0.1 M KOH, (d) CV curves of S/N/CNT in 0.1 M KOH, (e) The ECSAs of CNT, S/CNT, N/CNT and S/N/CNT



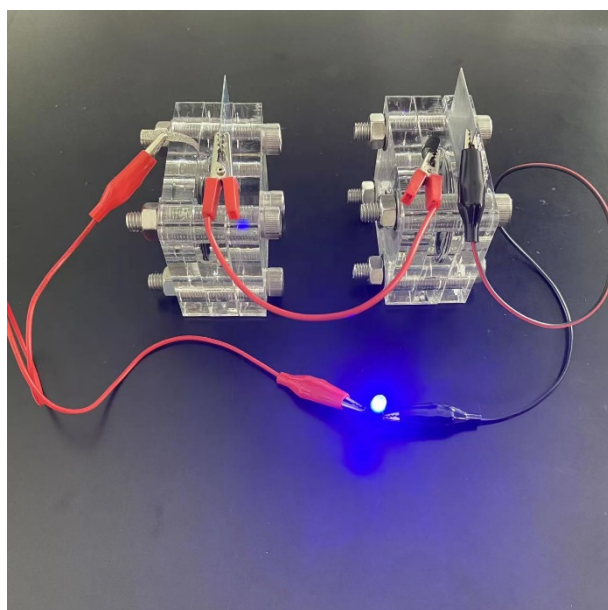
**Fig. S6** EIS of CNT, S/CNT, N/CNT and S/N/CNT in 0.1 M KOH



**Fig. S7** Opencircuit voltages of commercial Pt/C (left) and S/N/CNT (right) based primary liquid ZABs



**Fig. S8** Rate performances of ZABs with the S/N/CNT and Pt/C electrocatalysts.



**Fig. S9** Two S/N/CNT-based ZABs were connected in series to supply adequate



voltage to power the colored LEDs (2.5 V)