

## Supplementary Materials

### **Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub>/Fe nanoparticles anchored on N-doped hierarchically porous carbon nanospheres as high-efficiency ORR electrocatalysts for rechargeable Zn-air batteries**

*Yali Wang<sup>a</sup>, Ruihui Gan<sup>a</sup>, Hao Liu<sup>a</sup>, Mahmut Dirican<sup>b</sup>, Chengbiao Wei<sup>a</sup>, Chang Ma*

*<sup>a, b, \*</sup>, Jingli Shi<sup>a, \*</sup>, Xiangwu Zhang<sup>b</sup>*

*<sup>a</sup> Tianjin Municipal Key Lab of Advanced Fiber and Energy Storage Technology,  
Tiangong University, Tianjin 300387, P. R. China.*

*<sup>b</sup> Fiber and Polymer Science Program, Department of Textile Engineering, Chemistry  
and Science, Wilson College of Textiles, North Carolina State University, Raleigh,  
North Carolina 27695-8301, United States*

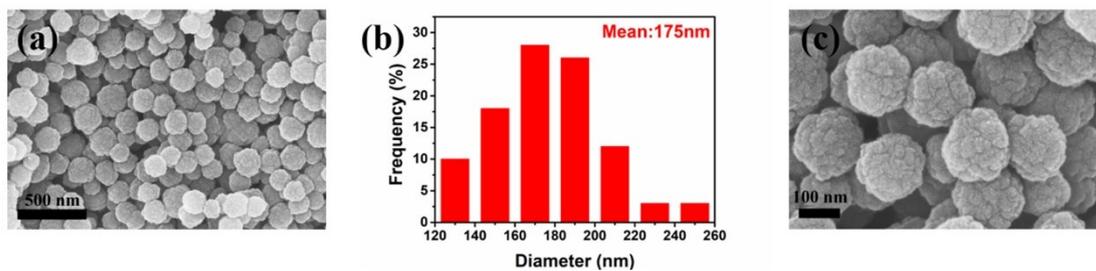


Figure S1. SEM images of the Fe-CNSs-C sample.

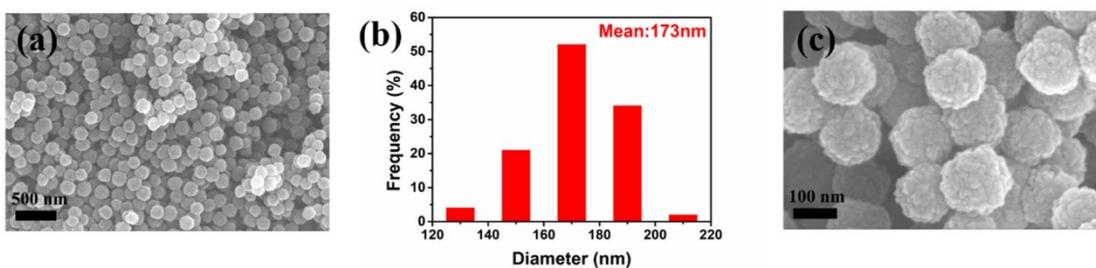


Figure S2. SEM images of CNSs-N sample.

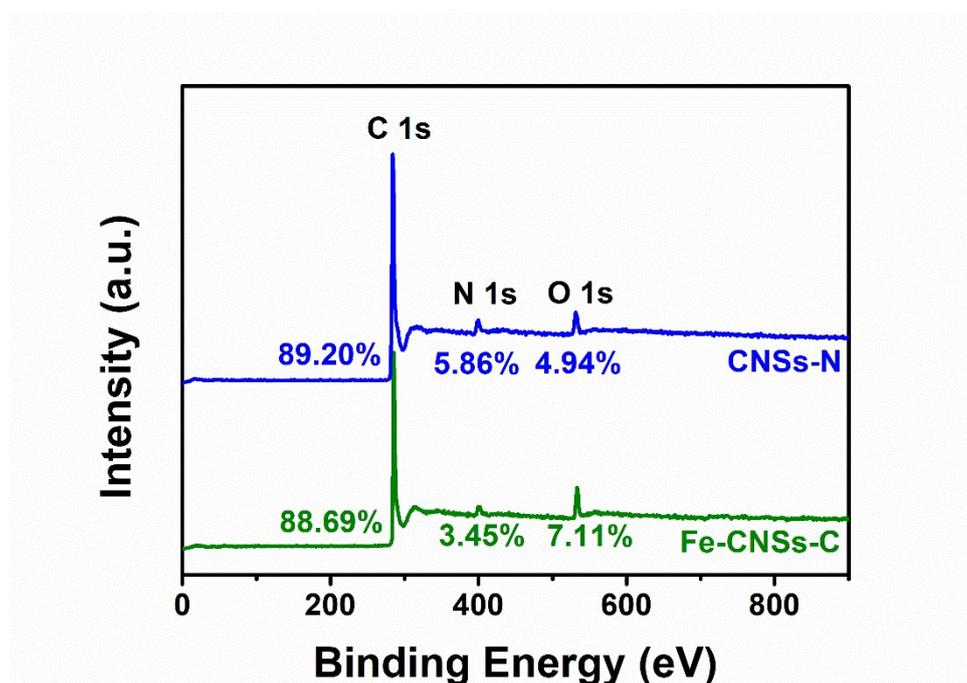
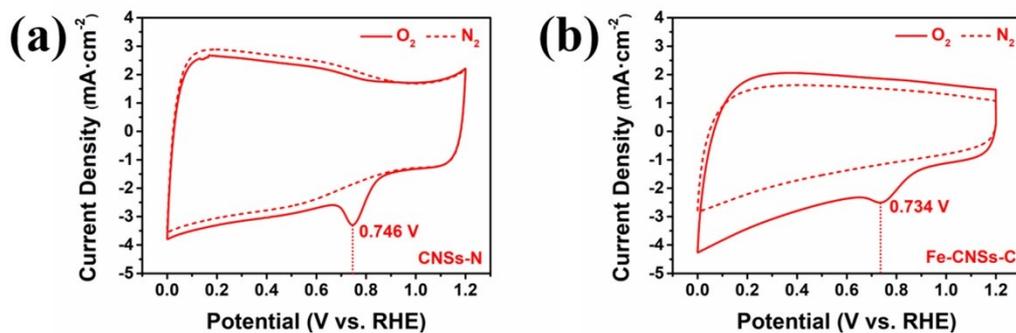
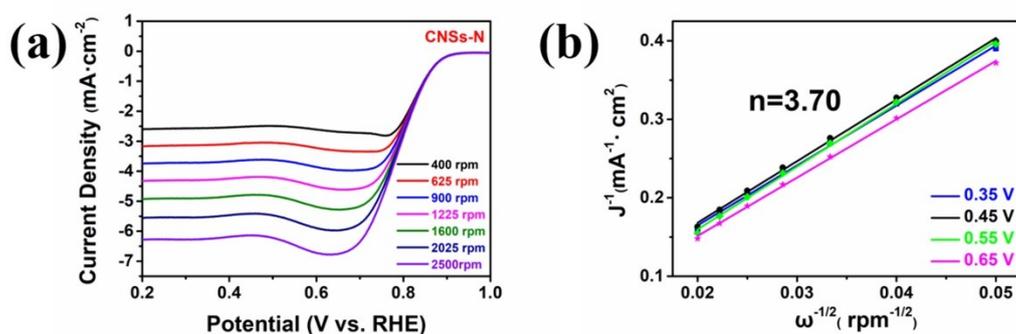


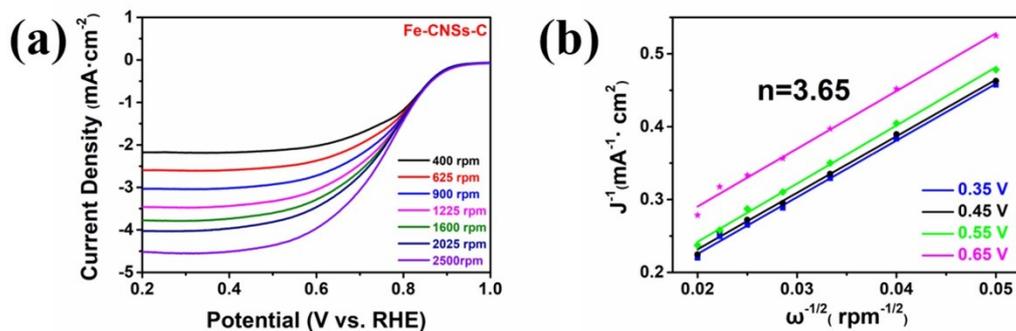
Figure S3. Survey spectra of CNSs-N and Fe-CNSs-C.



**Figure S4.** CVs of CNSs-N and Fe-CNSs-C.



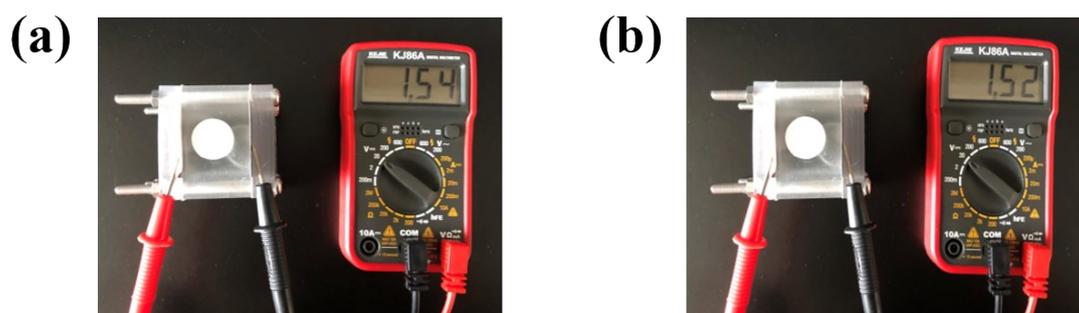
**Figure S5.** (a) LSV curves of CNSs-N at a scan rate of  $10 \text{ mV} \cdot \text{s}^{-1}$  and various rotating rates from 400 to 2500 rpm. (b) K-L plots of CNSs-N derived from LSV curves at various potentials.



**Figure S6.** (a) LSV curves of Fe-CNSs-C at a scan rate of  $10 \text{ mV} \cdot \text{s}^{-1}$  and various rotating rates from 400 to 2500 rpm. (b) K-L plots of Fe-CNSs-C derived from LSV curves at various potentials.

**Table S1.** The electrocatalytic performances of Fe-CNSs-N, Fe-CNSs-C, CNSs-N and Pt/C for oxygen reduction reaction in alkaline electrolytes.

Catalyst	$E_{\text{onset}}$ (V vs RHE)	$E_{1/2}$ (V vs RHE)	$J_K$ ( $\text{mA}\cdot\text{cm}^{-2}$ )
Pt/C	0.947	0.828	5.52
Fe-CNSs-N	0.948	0.835	5.17
Fe-CNSs-C	0.937	0.765	3.81
CNSs-N	0.910	0.809	4.79



**Figure S7.** The photographs of the open-circuit voltage of the Zn-air batteries using Fe-CNSs-N (a) and commercial Pt/C (b) as air electrodes measured by multimeter.