**Supporting Information** 

# Self-Templated Synthesis of Heavily Nitrogen-Doped Hollow Carbon Spheres

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### **Preparation of NHCSs**

All the materials were used as received without further purification. ZnNCN powder was synthesized according to the previous method<sup>1</sup>. In a typical synthesis, 29 mmol zinc chloride (ZnCl<sub>2</sub>, 98%, Shanghai AiBi Ltd.), 49 mmol cyanamide (H<sub>2</sub>NCN, 95%, J&K Scientific Ltd.), 12 ml aqueous ammonia (NH<sub>4</sub>OH, 25 wt%) and 50 ml distilled water were mixed and stirred for 3 h, and after that, a white precipitate was obtained. Then the precipitate was filtered and washed with distilled water several times to remove the residual H<sub>2</sub>NCN and NH<sub>4</sub>OH, and the byproduct NH<sub>4</sub>Cl. Finally, the white precipitate was dried in a vacuum at 80 °C for 12 hours.

ZnNCN powder (0.2 g) was placed inside an evacuated quartz tube. Then the tube was kept inside a two-zone furnace; one zone of the furnace was heated to 1100 °C at a rate of 1 °C min<sup>-1</sup> and held for 240 min, and at the same time the other zone was heated to 700 °C in 1200 min and held for 140 min. After naturally cooling to room temperature the NHCSs were obtained in the low-temperature zone.

The low N content of NHCSs was obtained by heating the pristine NHCSs in 1100 °C for 6 hours in a vacuum. Acid treatment of the pristine NHCSs was carried out in 2 M HNO<sub>3</sub> for 6 hours to remove residual zinc.

### **Characterization of NHCSs**

The morphology of NHCSs was characterized by scanning electron microscope (SEM, JEOL JSM-6501), field-emission scanning electron microscope (FESEM, JEOL 7800F), and transmission electron microscope (TEM, JEOL 2100F). Phase analysis was performed by X-ray diffraction (XRD) using a Bruker D8 ADVANCE

diffractometer with Cu-K $\alpha$  (1.5406 Å) irradiation. X-ray photoelectron spectroscopy (XPS) was obtained using an RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K $\alpha$  radiation (hv =1253.6 eV), where containment carbon (C 1s =284.6 eV) is calibrated. Raman spectra were collected with a Thermal Dispersive Spectrometer using a 10 mW laser with an excitation wavelength of 532 nm. Fourier-transform infrared spectroscopy (FTIR) measurements were carried out in a Spotlight 400. The ORR data were collected with the electrochemical station (CHI 760E) and the rotating-disk electrode system (Pine Research Instrumentation, USA). The Brunauer-Emmett-Teller (BET) isotherm was obtained by nitrogen adsorption and desorption tests at 77 K on an ASAP 2460 system, and the pore size distribution was determined by Barret-Joyner-Halenda (BJH) analysis.

#### Electrocatalytic measurement of NHCSs toward ORR

Typically, NHCSs (5 mg) were added into 1 ml mixture of Nafion (5 wt%, Alfa Aesar) and ethanol. The weight ratio of Nafion and ethanol was 1:24. Then the mixture was ultrasonicated for 2 h to form a homogeneous ink. The rotating disk electrode (RDE) was washed with ethanol and water after being polished with 1  $\mu$ m and 0.05  $\mu$ m alumina. Then 10  $\mu$ l of the well-dispersed ink was dropped on the surface of the glass carbon (4 mm in diameter) of the RDE and dried under room temperature. The catalyst loadings were ~ 0.26 mg cm<sup>-2</sup>.

All the ORR performances were tested with a conventional three-electrode cell on an electrochemical workstation (CHI 760E). A graphite rod and a Hg/HgO (1 M KOH solution) electrode were used as counter and reference electrodes, respectively. The catalyst coated RDE served as the working electrode. The electrolyte was 0.1 M KOH aqueous solution. Before the experiments,  $O_2$  (or  $N_2$ ) was purged into the electrolyte in the cell at least 30 min to saturate it with  $O_2$  (or  $N_2$ ). All the experiments were carried out at 25 °C. Except for otherwise stated, all the potentials measured against reference electrodes were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation:

$$E_{\rm RHE} = E_{\rm Hg/HgO} + 0.0591 \rm pH + E_{\rm Hg/HgO}^{\Theta}$$
(1)

where  $E_{\text{Hg/HgO}}$  is the potential measured experimentally versus a Hg/HgO (1 M KOH solution) electrode and  $\stackrel{\Theta}{\text{E}_{\text{Hg/HgO}}}$  is the standard electrode potential (0.098 V).

The cyclic voltammograms (CV) experiments were conducted in  $O_2$  (or  $N_2$ ) saturated 0.1 M KOH solution with a scan rate of 100 mV s<sup>-1</sup> from 0.2 V to 1.2 V vs. RHE. The polarization curves were collected from 0.2 V to 1.0 V vs. RHE in the  $O_2$ -saturated 0.1 M KOH solution at 5 mV s<sup>-1</sup> under rotation speeds of 1600, 1225, 900, 625 and 400 rpm.

The number of electrons transferred in the ORR reaction (*n*) was calculated by Koutecky–Levich (K–L) equation:

$$\frac{1}{J} = \frac{1}{J_{\rm L}} + \frac{1}{J_{\rm K}} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_{\rm K}}$$
(2)  

$$B = 0.2n \text{FC}_0 (\text{D}_0)^{2/3} \upsilon^{-1/6}$$
(3)

where J is the measured current density,  $J_{\rm L}$  is the diffusion-limited current density

and  $J_{\rm K}$  is the kinetic-limited current densities.  $\omega$  is the electrode rotation rate in rpm, F is the faraday constant (96 485 C mol<sup>-1</sup>), C<sub>0</sub> is the bulk concentration of oxygen (1.2 $\swarrow$  10<sup>-6</sup> mol cm<sup>-3</sup>), D<sub>0</sub> is the diffusion coefficient of O<sub>2</sub> in 0.1 M KOH (1.9 $\textdegree$  10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>),  $\upsilon$  is the kinetic viscosity of the electrolyte (0.01 cm<sup>2</sup> s<sup>-1</sup>).

The stability of the catalyst was tested with an accelerated degradation test protocol according to the previous report<sup>2</sup>, namely, 1000 cycles CVs ( $0.6 \sim 1.2 \text{ V} vs. \text{ RHE}$ ) in N<sub>2</sub>-saturated 0.1 M KOH (50 mV s<sup>-1</sup>). After CV cycles, the polarization curves were collected at the same condition as before.



Figure S1. (A) FESEM image of ZnNCN and (B) its corresponding magnification in the red rectangle. (C) XRD pattern of ZnNCN; inset is the crystal structure of ZnNCN.(D) FTIR spectrum of ZnNCN.



Figure S2. XRD pattern of Zn(CN)<sub>2</sub>.



**Figure S3.** (A, B) TEM images of carbon nanotubes obtained at the high-temperature zone. (C) The Raman spectrum of the nanotubes. (D) The XPS spectrum of the nanotubes.



Figure S4. The diameter distribution of NHCSs (inset is the SEM image of the NHCSs).



Figure S5. (A, B) TEM images of the shell of the NHCSs.



**Figure S6.** (A, B, C) SEM images of NHCSs at different temperatures (1050 °C, 1100 °C, 1150 °C). (D, E, F) SEM images of NHCSs at different heating rates (1 °C min<sup>-1</sup>, 3 °C min<sup>-1</sup>, 5 °C min<sup>-1</sup>).



Figure S7. The XPS spectrum of NHCSs.

To gain more kinetics information of NHCSs, the ORR polarization curves at different rotation rates from 1600 to 400 rpm (Figure S8B) were measured to determine the transferred electron number (n) per oxygen molecule involved in the oxygen reduction on the basis of Koutecky–Levich (K–L) equation. As shown in Figure S8C, all the plots showed good linearity and the number of electrons transferred in the ORR reaction at 0.4 V, 0.5 V, 0.6 V is calculated from Figure S8C to be 2.59, 2.95, 3.25, respectively, indicating that the ORR involved both two- and four-electron pathways. Among several types of nitrogen, pyridinic N is considered to create the ORR active sites.<sup>3</sup> Thus the high nitrogen content in our sample, especially pyridinic N, may play a dominant part in the ORR activities.

Good stability toward ORR is also a critical property of catalysts. The ORR stability of NHCSs was tested according to an accelerated degradation test protocol described in experimental section. The stability analysis was obtained by comparing linear sweep voltammograms before and after the cycling protocol. As Figure S8D showed, the onset potentials were nearly no change. However, instead of remaining unchanged or decreasing, the measured current density increased from 3.2 mA cm<sup>-2</sup> before 1000 cycles to 4 mA cm<sup>-2</sup> after 1000 cycles, indicating an exceptional cycling stability.



**Figure S8.** (A) Cyclic voltammograms of NHCSs at a scan rate of 100 mV s<sup>-1</sup> in N<sub>2</sub>saturated and O<sub>2</sub>-saturated aqueous solutions of 0.1 M KOH. (B) The rotation ratedependent ORR polarization curves for NHCSs. (C) The Koutecky–Levich plots at different potentials based on (B). (D) ORR polarization curves at rotating speed of 1600 rpm before and after 1000 CV cycles.



Figure S9. The comparison of ORR polarization curves between low and high nitrogen

content of NHCSs.



Figure S10. The comparison of (A) XRD, (B) XPS, and (C) ORR polarization curves

before and after acid treatment of the NHCSs.

Carbon and Nitrogen Sources	Templates	Carbonization	Total	
		Temperature	Ν	Ref.
		(°C)	(wt%)	
Dopamine hydrochloride	Polystyrene	800	2.92	4
	spheres			
Ionic liquid	Silica spheres	800	3.2	5
3-Aminophenol/formaldehyde	Silica spheres	600	6.86	6
Dopamine	Silica spheres	600	8.6	7
Resorcinol/formaldehyde/	Silica spheres	750	12.4	8
ethylenediamine				
Resorcinol/formaldehyde/	Silica spheres	600	14.8	9
melamine				
ZnNCN	Self-template (Zn)	1100	12.45	This work

**Table S1.** A comparison of carbon and nitrogen sources, templates, and total nitrogen

 content from the literature.

## References

- K. Morita, G. Mera, K. Yoshida, Y. Ikuhara, A. Klein, H.-J. Kleebe and R. Riedel, Solid State Sci, 2013, 23, 50.
- 2 Y. Shao, S. Zhang, M. H. Engelhard, G. Li, G. Shao, Y. Wang, J. Liu, I. A. Aksay and Y. Lin, *J. Mater. Chem.*, 2010, **20**, 7491.

- 3 D. H. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo and J. Nakamura, *Science*, 2016,
  351, 361.
- 4 S. Zhao, T. Yan, H. Wang, G. Chen, L. Huang, J. Zhang, L. Shi and D. Zhang, *Appl. Surf. Sci.*, 2016, **369**, 460.
- 5 A. Chen, Y. Yu, H. Lv, Y. Wang, S. Shen, Y. Hu, B. Li, Y. Zhang and J. Zhang, J. Mater. Chem. A, 2013, 1, 1045.
- 6 A. Chen, Y. Li, Y. Yu, S. Ren, Y. Wang, K. Xia and S. Li, *J. Alloy. Compd.*, 2016, 688, 878.
- 7 S.-W. Bian, S. Liu, M.-X. Guo, L.-L. Xu and L. Chang, RSC Adv., 2015, 5, 11913.
- 8 Y. Qu, Z. Zhang, K. Du, W. Chen, Y. Lai, Y. Liu and J. Li, Carbon, 2016, 105, 103.
- 9 S. Feng, W. Li, Q. Shi, Y. Li, J. Chen, Y. Ling, A. M. Asiri and D. Zhao, *Chem. Commun.*, 2014, **50**, 329.