Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information for

A Large-scale Synthesis of Heteroatom (N and S) co-doped Hierarchically Porous Carbon (HPC) Derived from Polyquaternium for Superior Oxygen Reduction Reactivity

Mingjie Wu[a], Jinli Qiao[a,d*], Kaixi Li[c], Xuejun Zhou[a], Yuyu Liu[b,e*], Jiujun Zhang[d,f]

[a]*College of Environmental Science and Engineering, Donghua University, 2999 Ren'min North Road, Shanghai 201620, P. R. China, qiaojl@dhu.edu.cn*

[b]*College of Environmental Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, P. R. China*

[c]*Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, P. R. China*

[d]*Institute of Functional Materials, Donghua Universtiy, 2999 Ren'min North Road, Shanghai 201620, P. R. China*

[e]*Multidisciplinary Research on the Circulation of Waste Resources,Graduate School of Environmental Studies, Tohoku University, Aramaki, aza Aoba 6-6-11, Aoba-ku, Sendai 980-8579, Japan, liu@mail.kankyo.tohoku.ac.jp*

[f]*Energy, Mining & Environment, National Research Council of Canada, Vancouver, BC, Canada, Jiujun.Zhang@nrc-cnrc.gc.ca*

The peroxide percentage (H_2O_2%) was determined from RRDE measurements based on the disk current (I_d) and ring current (I_r) via the following equation:

$$H_2O_2\% = 100 \times \frac{2I_r / N}{I_d + I_r / N}$$

□ □

The electron transfer number (n) was based on the following equation:

$$n = \frac{4I_d}{I_d + I_r / N}$$ □

□

where N = 0.36 is the current collection efficiency of Pt ring, which is calibrated in 0.1M KOH with a 10 mM $K_3Fe(CN)_6$ electrolyte.

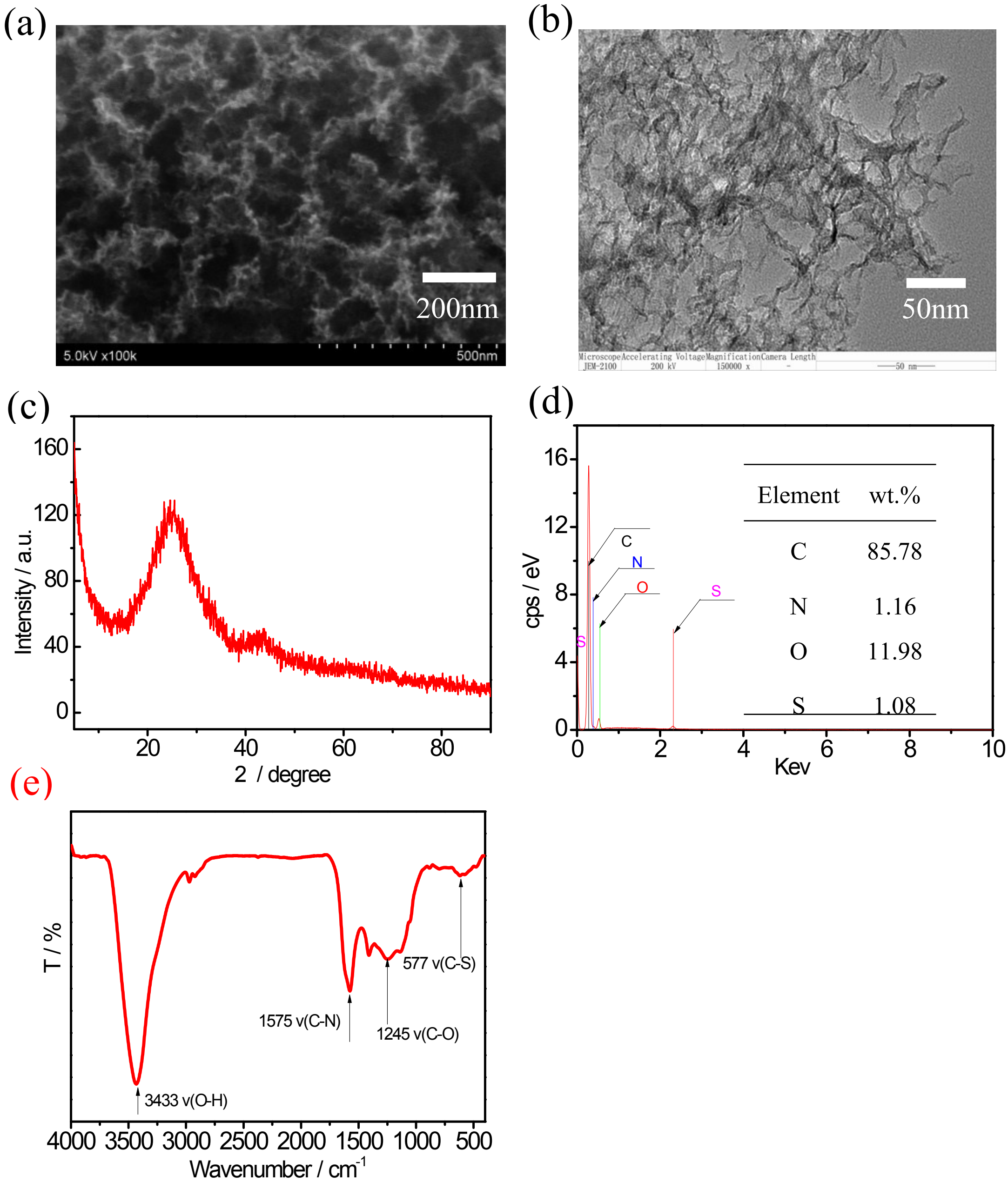

Fig. S1 (a) SEM image and (b) TEM image of N-S-HPC catalyst with different magnifications, showing the highly porous structures. (c) XRD pattern of N-S-HPC sample. (d) EDS spectrum of the N-S-HPC sample (Insert: composition of the N-S-HPC). (e) FT-IR spectra of N-S-HPC in the range of 4000–400 cm^{-1}.

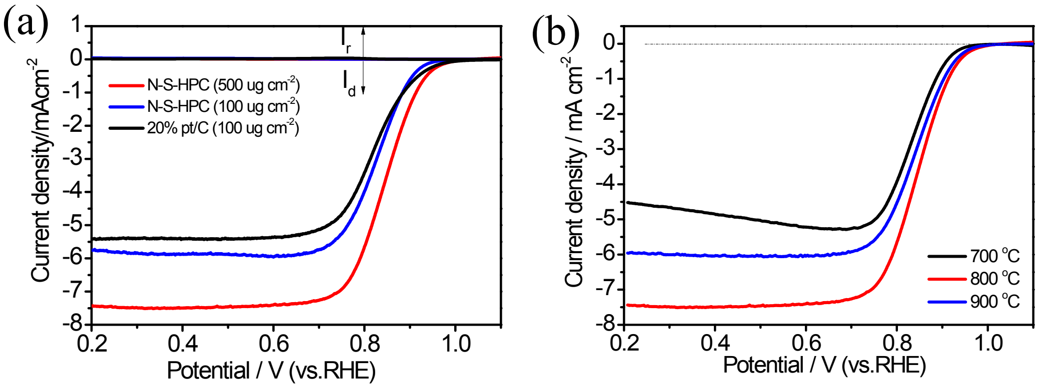

Fig. S2 (a) RRDE test of the ORR on N-S-HPC and Pt/C catalysts in an O_2-saturated 0.1 M KOH electrolyte at a rotation rate of 1600 rpm; (b) Linear sweep ORR voltammetric curves for N-S-HPC catalysts obtained at different heat-treatment temperatures, measured in O_2-saturated 0.1 M KOH solution at a scan rate of 5 mV s^{-1}.

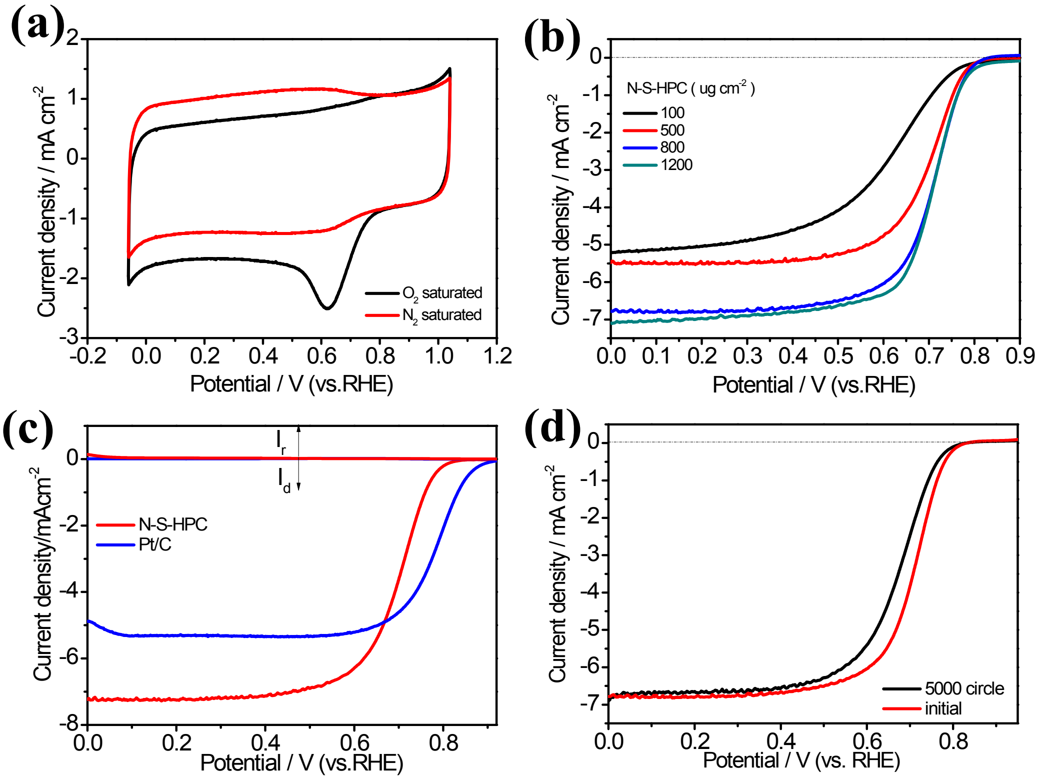

Fig. S3 (a) Cyclic voltammograms of N-S-HPC in N_2- and O_2-saturated 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1} (100 μg cm^{-2}); (b) Linear sweep voltammograms of N-S-HPC catalysts with different loadings in an O_2-saturated 0.5 M H_2SO_4 electrolyte at a rotation rate of 1500 rpm; (c) RRDE test of the ORR on N-S-HPC and Pt/C catalyst in an O_2-saturated 0.5 M H_2SO_4 electrolyte at a rotation rate of 1600 rpm. The loading was 0.5 mg cm^{-2} for N-S-HPC and 0.1 mg cm^{-2} for Pt/C; (d) Linear sweep voltammograms of N-S-HPC on a rotating disk electrode (1500 rpm) before and after 5000 cycles in O_2-saturated 0.1 M H_2SO_4 at a scan rate of 5 mV s^{-1}.

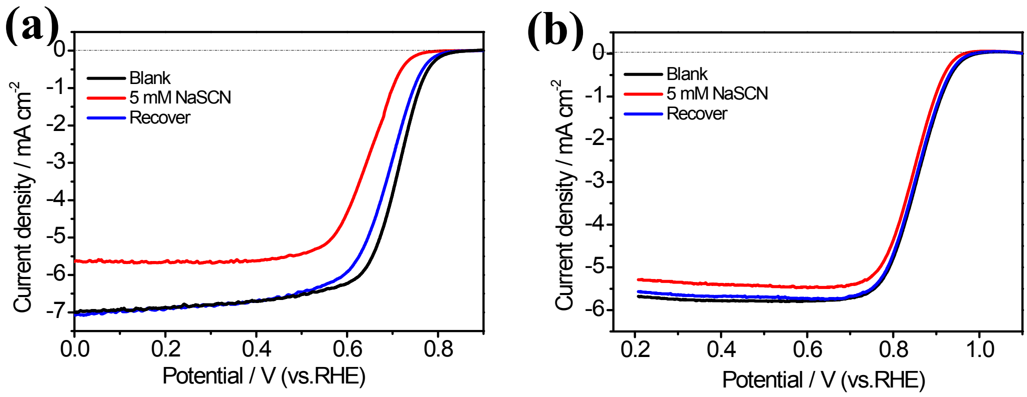

Fig. S4 (a) Linear sweep voltammograms of N-S-HPC on a rotating disk electrode (1500 rpm) in O_2-saturated 0.5 M H_2SO_4 (with and without NaSCN) at a scan rate of 5 mV s^{-1}. (b) Linear sweep voltammograms of N-S-HPC on a rotating disk electrode (1500 rpm) in O_2-saturated 0.1 M KOH (with and without NaSCN) at a scan rate of 5 mV s^{-1}.

Supplementary Table 1. Summary of reported ORR performance of heteroatom-doped carbon catalysts (All catalysts were tested in 0.1 M KOH, rpm = 1600).

Catalyst	Catalyst loading (mg cm^{-2})	Half-wave potential (V vs. RHE)	Current density at 0.8 V (mA cm^{-2})	Reference
Meso/micro-PoPD	0.1 0.5	0.85 0.87	4.32 4.95	*Nat. Commun.* **2014**, 5, 4973
Pt/C	0.1	0.85	3.98	
Hierarchically porous N-doped carbon nanoflakes	0.1 0.25	0.80 0.86	2.0 4.5	*Carbon,* **2014**, 78, 60
N and S dual-doped graphene	0.42	0.67	< 2.0	*Adv. Mater.* **2013**, 25, 6226
B/N co-doped carbon nanosheets	--	0.69	< 2.0	*J. Mater. Chem. A,* **2014**, 2,7742
Pt/C		0.79	2.7	
nitrogen-doped carbon nanosheets	0.6	0.83	3.2	*Angew. Chem. Int. Ed.* **2014**, 53, 1570
Carbon nanotube–graphene (NT–G) complexes	0.485	0.87	5.0	*Nat Nanotechnol.* 2012, 7, 394
Cobalt Porphyrin-Based Conjugated Mesoporous Polymers	0.6	0.64	4.8	*Adv. Mater.* **2014**, 26, 1450
Pt/C	0.15	0.80	2.5	
Heteroatom (N and S) co-doped hieratchically porous carbons (N-S-HPC)	**0.1** **0.5**	**0.83** **0.87**	**4.1** **5.8**	**This work**
Pt/C	**0.1**	**0.82**	**3.42**	

Supplementary Table 2. Summary of reported ORR performance of heteroatom-doped carbon catalysts (All catalysts were tested in 0.5 M H_2SO_4, rpm = 1600).

Catalyst	**Catalyst loading (mg cm^{-2})**	**Half-wave potential (V vs. RHE)**	**Current density at 0.5 V (mA cm^{-2})**	**Reference**
Meso/micro-PoPD	0.5	0.71	3.8	*Nat. Commun.* **2014**, 5, 4973
Hierarchically porous N-doped carbon nanoflakes	0.25	0.47	4.5	*Carbon,* **2014**, 78, 60
Mesoporous Fe-N-Doped Carbon Nanofibers	0.6	0.58	3.7	*Angew. Chem. Int. Ed.* **2015**, 54, 8179
Cobalt Porphyrin-Based Conjugated Mesoporous Polymers	0.6	0.64	4.8	*Adv. Mater.* **2014**, 26, 1450
Pt/C	0.15	0.78	5.2	
Nitrogen-doped carbon nanosheets	0.6	0.56	3.5	*Angew. Chem. Int. Ed.* **2014,** 53, 1570
Carbon nanotube–graphene (NT–G) complexes	0.485	0.76	5.6	*Nat Nanotechnol.* 2012, 7, 394
Heteroatom (N and S) co-doped hieratchically porous carbons (N-S-HPC)	**0.5** **0.8**	**0.71** **0.73**	**6.2** **6.9**	**This work**
Pt/C	**0.1**	**0.73**	**5.3**	

Supplementary Table 3: Peak power density of primary Zn-air batteries with several key parameters extracted from literatures.

ORR catalyst used	Zn electrode/ electrolyte	Current Density @ V = 1.0 V ($mAcm^{-2}$)	Peak power density ($mWcm^{-2}$)	Reference
CoO/N-CNT	Zn foil/6M KOH	197	265	*Nat Commun.***2013**, 4, 1805
MnOx/Ketjenblack carbon	Zn powders/6M KOH	120	190	*Nano Lett.* **2011**, 11, 5362
MnO*x*/C	zinc plate/6 M KOH	97	122	*Int J Hydrogen Energ*, **2014**, 39, 3423
Mn_3O_4/Graphene	Zn powders/-	70	120	*Energy Environ. Sci.* **2011**, 4, 4148
α-MnO_2/XC72	zinc plate/6 M KOH	40	67.5	*J of Power Sources,* **2011**,6, 108
N-doped CNTs	zinc plate/6 M KOH	50	69.5	*Electrochim. Acta,* **2011**, 56, 5080
N-doped porous carbon nanofibers	zinc plate/6 M KOH	150	194	*J. Power Sources,* **2013**, 243, 267
N-S-HPC	**zinc plate /6 M KOH**	**317**	**536**	**This work**