Supporting Information

Synthesis of B-doped hollow carbon spheres as efficient non-metal catalyst for oxygen reduction reaction

Hui-Jia Lu, Ying Li, Lin-Qun Zhang, He-Nan Li, Zhi-Xin Zhou, An-Ran Liu, Yuan-Jian Zhang, Song-Qin Liu**

Jiangsu Province Hi-Tech Key Laboratory for Bio-medical Research, School of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, China. Fax: +86-25-52090618; Tel: +86-25-52090613; E-mail address: yingli@seu.edu.cn; liusq@seu.edu.cn.

(a) (b)

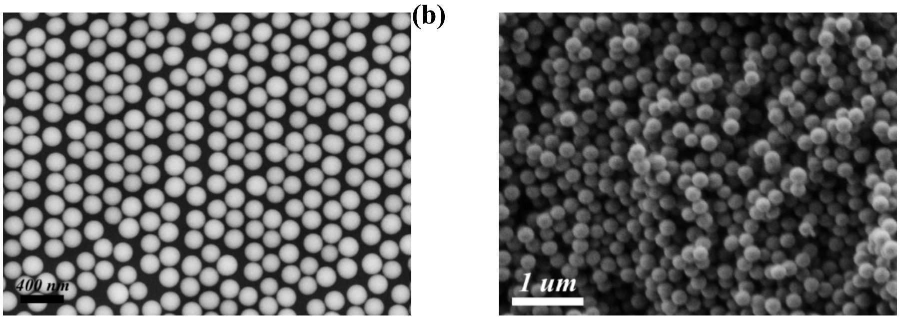

Fig. S1 SEM images of (a) the colloidal SiO_2 nanospheres prepared by a classical Stöber method, (b) boron doped carbon spheres after the hydrothermal reaction.

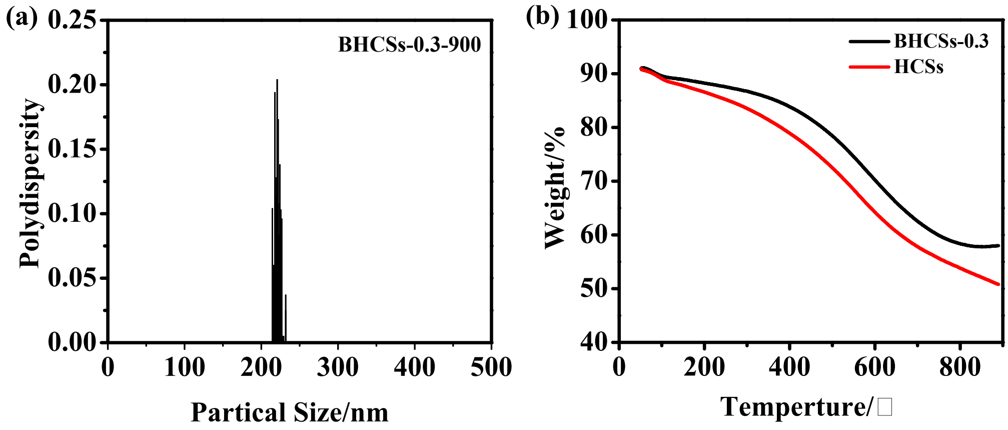

Fig. S2 (a) The DLS data of the BHCSs-0.3-900 nanospheres. (b) TG curve of the HCSs and BHCSs-0.3 at a heating rate of 20 °C min^{-1} in a N_2 atmosphere.

The carbonization of the samples was characterized by TG analyses (Fig. S2b). In the nitrogen atmosphere, a three-step weight loss process could be observed for both HCSs and BHCSs. The first step is under 100 ºC with a 1.83% weight loss due to the volatilization of water. The second step spans from 100 ºC to 350 ºC with a 3.91% weight loss due to the release of the monomers that did not participate in the reaction. The majority of chemicals decomposition takes place from 400 ºC~900 ºC, this weight loss may be attributed to a suite of complex chemical reactions, involving bond formation and crosslinking,[24] which result in the destruction of main chain and the release of small gases (CO, CO_2, CH_4 and H_2).

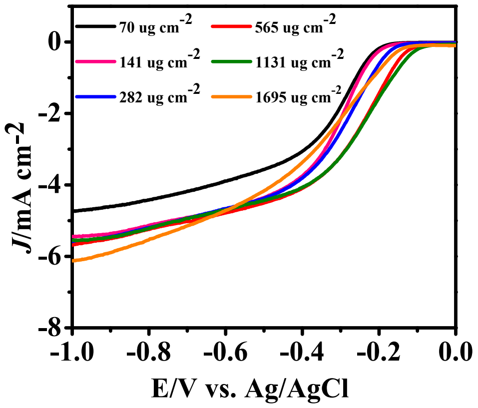

Figure S3 Polarization curves of BHCSs-0.3-900 with different mass loadings.

The Koutecky–Levich equations (equation (1)–(3)).

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

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

$J_K = nFkC_0$ (3)

Where, J is the measured current density, J_K and J_L are the kinetic and diffusion limiting current densities, ω is the angular velocity of the rotating electrode. n is the number of electrons exchanged per oxygen molecule, F is the Faraday constant (F=96485 C mol^{-1}), and k is the electron transfer rate constant, v is the kinematic viscosity of the electrolyte, D_0 is the oxygen diffusion coefficient, C_0 is the bulk concentration of oxygen. In this report, the electrolyte was O_2 saturated 0.1 M KOH, v, D_0 and C_0 were used as 0.01 cm^2 s^{-1} ,1.9×10-5 cm^2 s^{-1} and 1.2×10^{-3} M, respectively.

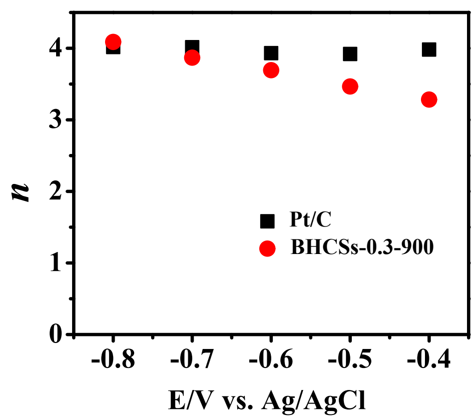

Fig.S4 The number of electrons exchanged per oxygen molecule of Pt/C and BHCSs-0.3-900 at different potentials from -0.4 to -0.8 V.

Table S1. Summary of heteroatom doped carbon materials as electrocatalyst for ORR

Catalyst	Synthesis method (precursors)	ORR performance		Ref.
		Heteroatom doped carbon materials	Pt/C	
Co-N- grapheme	Hydrothermal reaction (Grapheme oxide, urea and $CoCl_2$)	E_{onset} (V vs. Ag/AgCl) = -0.053 J_k (mA cm^{-2}) = 3.158 (at - 0.7 V) n = 3.97 (from -0.3 to -0.5 V)	E_{onset} (V vs. Ag/AgCl) = 0.045 J_k (mA cm^{-2}) = 3.081 (at - 0.7 V)	S1
N- carbon nanocables	Hydrothermal, thermal treatment (CNTs, glucose, melamine)	E_{onset} (V vs. Ag/AgCl) = -0.114 $E_{1/2}$ (V vs. Ag/AgCl) = -0.184 n = 3.97	$E_{1/2}$ (V vs. Ag/AgCl) = -0.142 n = 3.97	S2
B- mesoporous carbons	Thermal treatment (sucrose, 4-hydroxyphenylboronic acid)	E_{onset} (V vs. Ag/AgCl) = -0.16 n = 3.86 (at -0.5 V)	E_{onset} (V vs. Ag/AgCl) = -0.07 n = 4 (at -0.5 V)	S3
B- carbons	Thermal treatment (tetraphenylboron sodium)	E_{onset} (V vs. NHE) = -0.005 J_k (mA cm^{-2}) = 11.0 n = 3.73 (at -0.3 V)	E_{onset} (V vs. NHE) = 0.15 J_k (mA cm^{-2}) = 16.8	S4
P- mesoporous carbons	Thermal treatment (triphenylphosphine, phenol)	E_{onset} (V vs. Ag/AgCl) = -0.11 n = 3.9 (at -0.25 V)	E_{onset} (V vs. Ag/AgCl) = -0.06 n = 4.0 at -0.25 V	S5
P- carbons	Sol–gel polymerization, thermal treatment (resorcinol, formaldehyde, H_3PO_4)	E_{onset} (V vs. Ag/AgCl) = -0.13 n = 3.0-3.78 (from -0.3 to -0.8 V)	E_{onset} (V vs. Ag/AgCl) = -0.01 n = 3.9-3.96 (from -0.3 to -0.8 V)	S6
S- grapheme	Thermal treatment (graphite oxide, H_2S)	E_{onset} (V vs. Ag/AgCl) = -0.165 J_k (mA cm^{-2}) = 14 (at -0.7 V) n = 2.4 (at -0.8 V)	Not mentioned	S7
B-hollow carbon spheres	Hydrothermal, thermal treatment (resorcinol, formaldehyde , 4-hydroxyphenylboronic acid)	E_{onset} (V vs. Ag/AgCl) = -0.1 J_k (mA cm^{-2}) = 6.91 (at -0.6 V) n = 3.7 (at -0.6 V)	E_{onset} (V vs. Ag/AgCl) = -0.09 J_k (mA cm^{-2}) = 7.64 (at -0.6 V) n = 3.9 (at -0.6 V)	***This work***

Supporting reference:

[s1] B. Zheng, J. Wang, F. B. Wang, X. H. Xia. *J. Mater. Chem. A*, 2014, **2**, 9079-9084.

[s2] W. J. Jiang, J. S. Hu, X. Zhang, Y. Jiang, B. B. Yu, Z. D. Wei, L. J. Wan. *J. Mater. Chem. A*, 2014, **2**, 10154-10160.

[s3] X. J. Bo, L. P. Guo. *Phys. Chem. Chem. Phys.*, 2013, **15**, 2459-2465.

[s4] G. Jo, S. Shanmugam. *Electrochem. Commun.*, 2012, **25**, 101-104.

[s5] D. S. Yang, D. Bhattacharjya, S. Inamdar, J. Park, J. S. Yu. *J. Am. Chem. Soc.*, 2012, **134**, 16127-16130.

[s6] J. Wu, Z. R. Yang, Q. J. Sun, X. W. Li, P. Strasser, R. Z. Yang. *Electrochima. Acta.*, 2014, **127**, 53-60.

[s7] M. Seredych, T. J. Bandosz. *Carbon*, 2014, **66**, 227-233.