Electronic Supplementary Information (ESI) for

Two-step synthesis of boron and nitrogen co-doped graphene as synergistically enhanced catalyst for oxygen reduction reaction

Jiapo Tai[†], Jiantong Hu[†], Zhongxin Chen and Hongbin Lu*

State Key Laboratory of Molecular Engineering of Polymers, and Department of Macromolecular Science, Fudan University, 220 Handan Road, Shanghai, 200433, China. Tel/Fax: 86-21-5566 4589. To whom correspondence should be addressed: hongbinlu@fudan.edu.cn.

This PDF includes:

1. O_{1s} XPS and C_{1s} XPS of NG and BNG;
2. A comparison between peaks designation in XPS N_{1s} and B_{1s} spectra;
3. TGA results of NG and BNG;
4. CV curves of commercial Pt/C catalyst in O_2/N_2-saturated 0.1 mol L^{-1} KOH;
5. A comparison of our BNG and other reported metal-free ORR catalysts;
6. K-L curve with reference plots for $2e^-$ and $4e^-$ pathways

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1. O_{1s} XPS and C_{1s} XPS of NG and BNG:

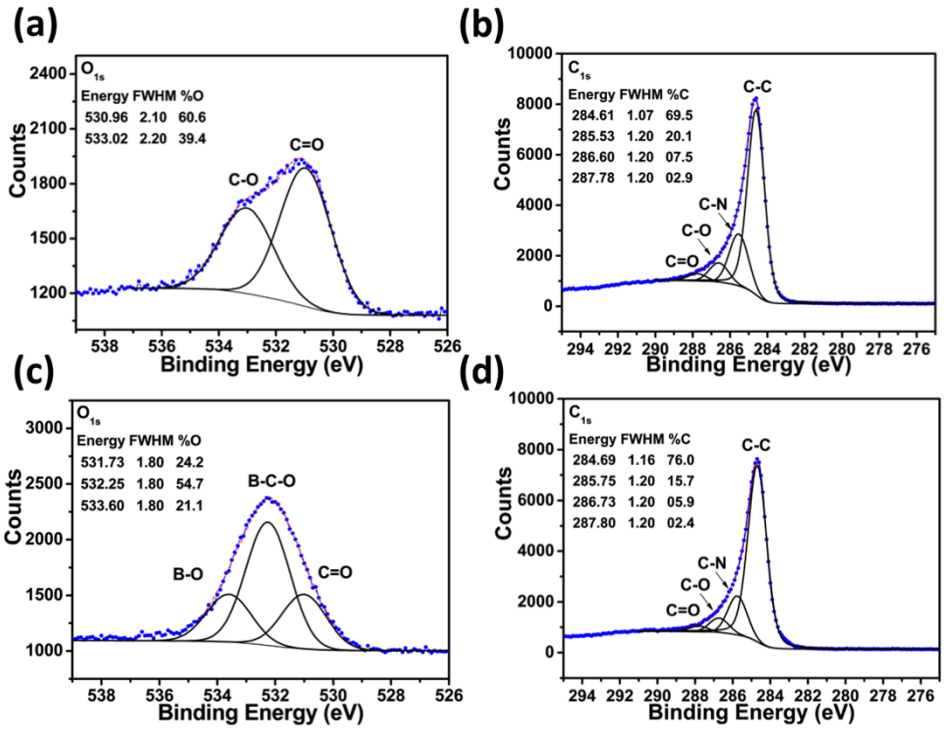

Fig. S1 (a) XPS-O_{1s} and (b) XPS-C_{1s} of NG; (c) XPS-O_{1s} and (d) XPS-C_{1s} of BNG

2. A comparison between peaks designation in N_{1s} and B_{1s} spectra:

XPS Measurements and Data Analysis:

X-ray photoelectron spectra (XPS) were carried out on a PHI Quantera SXM™ scanning X-ray Microprobe™ with monochromatic Al K_α radiation (hv = 1486.6 eV). The deconvolution of peaks was conducted using the XPS Peak processing software version 4.1 (Chemistry, CUHK), along with a Shirley background subtraction, a Gaussian sum function, and an iterative least-squares optimization algorithm. Before fitting, all binding energies were corrected according to the C_{1s} hydrocarbon peak at 284.8 eV. The position and full width half maximum (FWHM) of peaks in ***Figure 2 & S1*** *were determined on the basis of the results reported in literature and the spectrometer condition we used. The total fitting error is found to be smaller than 10 %.*

Peak Designations of N_{1s} spectra in the literature:

Table S1 A comparison of peaks designation in N1s spectra for N-doped or B, N co-doped graphene

N_{1s} spectrum	I	II	III	IV
Moieties	Pyridinic	Pyrrolic	Graphitic	--
Binding Energy	398.7	400.1	401.7	--
Reference	L. Fang, Y. Chen and L. Chen, *ACS Nano*, 2011, **5**, 9611-9618			
Moieties	Pyridinic	Pyrrolic	Graphitic	Pyridinic Oxide
Binding Energy	399.0	400.3	401.1	402.8
Reference	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**, 7491-7496.			
Moieties	Pyridinic	Pyrrolic	Graphitic	--
Binding Energy	398.6	399.8	401.0	--
Reference	G. Ma, R. Jia, J. Zhao, Z. Wang, C. Song, S. Jia and Z. Zhu, *J. Phys. Chem. C*, 2011, **115**, 25148–25154			
Moieties	Pyridinic	Pyrrolic	Graphitic	--
Binding Energy	398.5	400	401.5	--
Reference	C. V. Rao and Y. Ishikawa, *J. Phys. Chem. C*, 2012, **116**, 4340−4346			
Moieties	Pyridinic	Pyrrolic	Graphitic	Pyridinic Oxide
Binding Energy	398.7	400.3	401.4	402 ~ 405
Reference	D. Long, W. Li, L. Ling, J. Miyawaki, I. Mochida and S. H. Yoon, *Langmuir*, 2010, **26**, 16096–16102			
Moieties	Pyridinic	Pyrrolic	Graphitic	Pyridinic Oxide
Binding Energy	398.5	399.8	401.3	403.6
Reference	S. Li, Y. Hu, Q. Xu, J. Sun, B. Hou and Y. Zhang, *J. Power Sources*, 2012, **213**, 265-269			
Moieties	Pyridinic	Pyrrolic and Graphitic		Pyridinic Oxide
Binding Energy	398.6	400 ~ 402		402 ~ 404
Reference	C. H. Choi, S. H. Park and S. I. Woo, *ACS Nano*, 2012, **6**, 7084–7091			
Moieties	Pyridinic	Pyrrolic	Graphitic	--
Binding Energy	398.0	400.0	401.3	--
Reference	H. Wang, X. Bo, C. Luhana and L. Guo, *Electrochem. Commun.*, 2012, **21**, 5-8			
Moieties	Pyridinic	Pyrrolic	Graphitic	Pyridinic Oxide
Binding Energy	398.2	399.5	401.1	402.6
Reference	Z. H. Sheng, L. Shao, J. J. Chen, W. J. Bao, F. B. Wang and X. H. Xia, *ACS Nano*, 2011, **5**, 4350-4358.			
Moieties	Pyridinic	Pyrrolic	Graphitic	N-Oxide
Binding Energy	397.95	398.76	401.05	405.30
Reference	U. B. Nasini, V. G. Bairi, S. K., Ramasahayam, S. E. Bourdo, T. Viswanathan and A. U. Shaikh, *ChemElectroChem*, 2014, **1**, 573–579			

Moieties	Pyridinic	Amine	Pyrrolic	Protonated N or Graphitic
Binding Energy	398.6	399.4	400.1	401.4
Reference	P. Chen, T. Y. Xiao, Y. H. Qian, S. S. Li and S. H. Yu, Adv. Mater, 2013, 25, 3192-3196.			
Moieties	BN	Pyridinic	Graphitic	Pyridinic Oxide
Binding Energy	397.9	398.6	400.9	403.0
Reference	C. H. Choi, M. W. Chung, H. C. Kwon, S. H. Park and S. I Woo, *J. Mater. Chem. A*, 2013, **1**, 3694–3699			
Moieties	Pyridinic	Pyrrolic	Graphitic	Pyridinic Oxide
Binding Energy	398.1	399.6	401.2	403.0
Reference	Z. Lin, M. Song, Y. Ding, Y. Liu, M. Liu and C. Wong, *Phys. Chem. Chem. Phys.*, 2012, **14**, 3381–3387			
Moieties	Pyridinic	Pyrrolic	Graphitic	N-Oxide
Binding Energy	398.7	400.1	401.7	> 402
Reference	J. Wu, D. Zhang, Y. Wang, B. Hou, *J. Power Sources*, 2013. **227**, 185-190			
Moieties	Pyridinic	--	Graphitic	Pyridinic Oxide
Binding Energy	398.5	--	401.0	402.4
Reference	W. Wei, H. Liang, K. Parvez, X. Zhuang, X. Feng and K. Müllen, *Angew. Chem. Int. Edit.*, 2014, **126**, 1596 –1600.			
Moieties	Pyridinic	Pyrrolic	Graphitic	--
Binding Energy	398.4	399.8	401.7	--
Reference	This manuscript			

Peak Designations of B_s spectra in the literature:

Table S2 A comparison of peaks designation in B_{1s} spectra for B, N co-doped graphene

B_{1s} spectrum	**I**	**II**	**III**	**IV**
Moieties	BN_2C/BC_3	BC_2O/*h*-BN	BN_3/BCO_2	B-O
Binding Energy	189.5 eV	190.6 eV	192 eV	193 eV
Reference	J.-i. Ozaki, N. Kimura, T. Anahara and A. Oya, *Carbon*, 2007, **45**, 1847-1853.			
Moieties	--	BC_2O	BCO_2	B-O
Binding Energy	--	190.8 eV	191.5 eV	192.7 eV
Reference	J. Zhu, C. He, Y. Li, S. Kang and P. K. Shen, *J. Mater. Chem. A*, 2013, **1**, 14700-14705.			
Moieties	B-C	--	B-N	B-O
Binding Energy	189 eV	--	191 eV	192 eV
Reference	Y. Xue, D. Yu, L. Dai, R. Wang, D. Li, A. Roy, F. Lu, H. Chen, Y. Liu and J. Qu, *Phys. Chem. Chem. Phys.*, 2013, **15**, 12220-12226.			

Moieties	BC_3	BC_2O/BCO_2	--	B-O
Binding Energy	190 eV	191.2 eV	--	192.7 eV
Reference		This manuscript		

3. TGA results of NG and BNG:

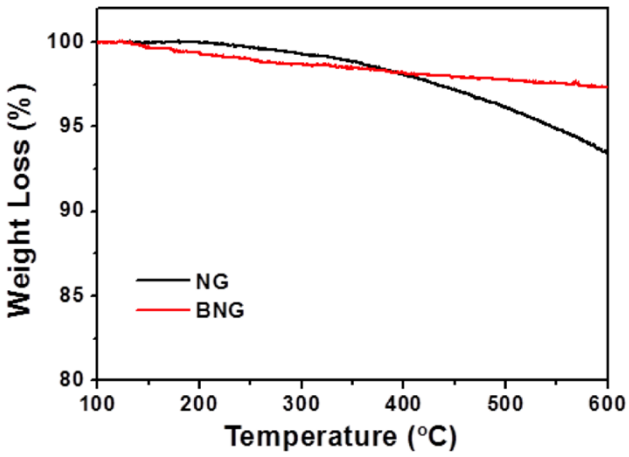

Fig. S2 TGA curves of NG and BNG (both samples were tested in nitrogen atmosphere , with the heating rate of 20 ℃ min^{-1})

4. CV curves of commercial Pt/C catalyst in 0.1 mol L^{-1} KOH:

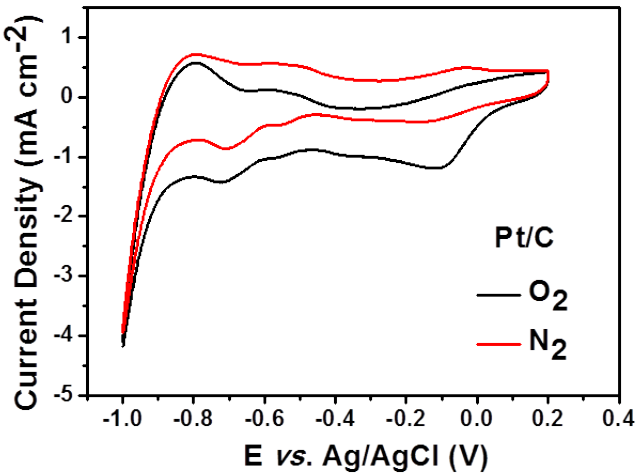

Fig. S3 CV curves of commercial Pt/C catalyst in O_2/N_2 saturated 0.1 mol L^{-1} KOH solution (scanning rate = 100 mV s^{-1})

5. A comparison of some metal-free ORR catalysts reported in literature:

Table S3 A comparasion of the major performances of some metal-free ORR catalysts reported in literature (all the electrocatalytic characterization were conducted in 0.1 mol L^{-1} KOH solution;

Items	Doping Levels	Catalyst Loading (mg cm^{-2})	Onset Potential (V *vs.* Ag/AgCl)	Current density at -0.8V (mA cm^{-2})	Ref.
N-doped graphene	N: 6.2 at.%	0.08	-0.3	3.6 (1200 rpm)	1
N-doped graphene	N: 7.25 at.%	0.14	-0.2	3.2 (1200 rpm)	2
N-doped graphene	N: 5 at.%	0.1	-0.2	4.5 (1900 rpm)	3
B-doped graphene	B: 3 at.%	Not mentioned	-0.12	5 (1600 rpm)	4
B,N co-doped graphene	N: 4.42 at.% B: 2.17 at.%	0.28	-0.16	5.2 (1500 rpm)	5
B,N co-doped graphene	N: 4.5 at.% B: 3 at.%	Not mentioned	-0.16	5.5 (1600 rpm)	6
B,N co-doped graphene	N: 11 at.% B:12 at.%	0.01 mg on the electrode	Not mentioned	5.1 (Rate not mentioned)	7
B,N co-doped graphene	N: 6.8 at.% B: 4.8 at.%	0.1	-0.17	5.5 (1600 rpm)	This study

the data in the table were calulated from the RDE test).

6. K-L curve with reference plots for $2e^-$ and $4e^-$ pathways:

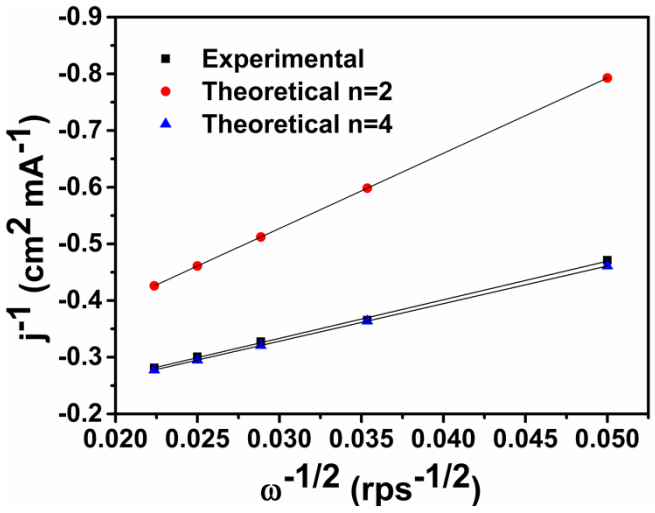

Fig. S4 Koutecky-Levich curve fitted from the data of RDE test. (potential = -0.4 V)

References:

1 Z. Lin, G. Waller, Y. Liu, M. Liu and C.-P. Wong, *Adv. Energy Mater.*, 2012, **2**, 884-888.

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7 S. Wang, L. Zhang, Z. Xia, A. Roy, D. W. Chang, J.-B. Baek and L. Dai, *Angew. Chem., Int. Ed.*, 2012, **51**, 4209-4212.