

Supporting Information

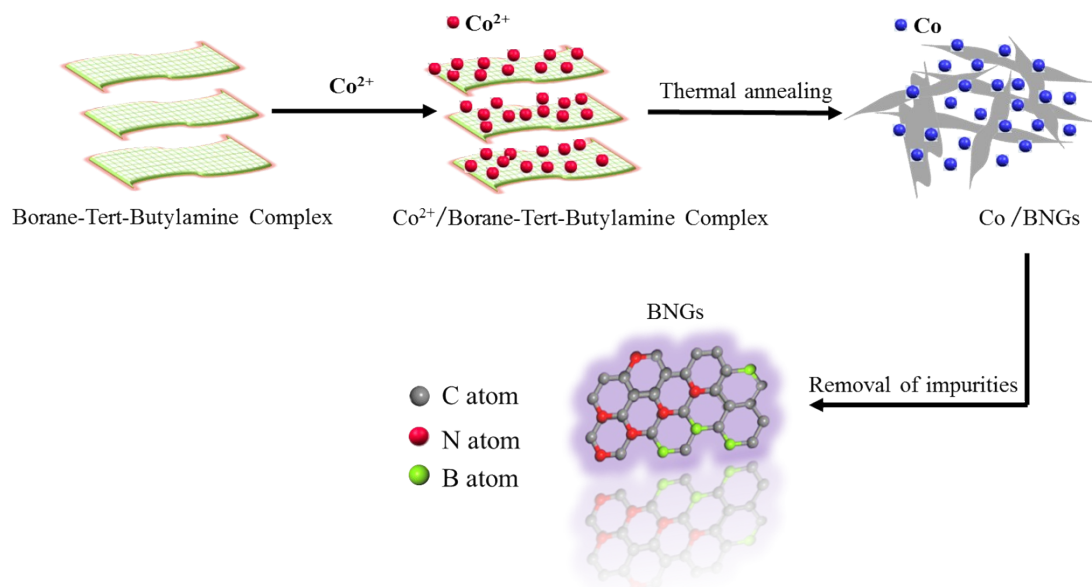
Crumpled nitrogen- and boron-dual-self-doped graphene sheets as an extraordinary active anode material for lithium ion batteries

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Scheme S1 Schematic illustration of the preparation procedure for NBGs.

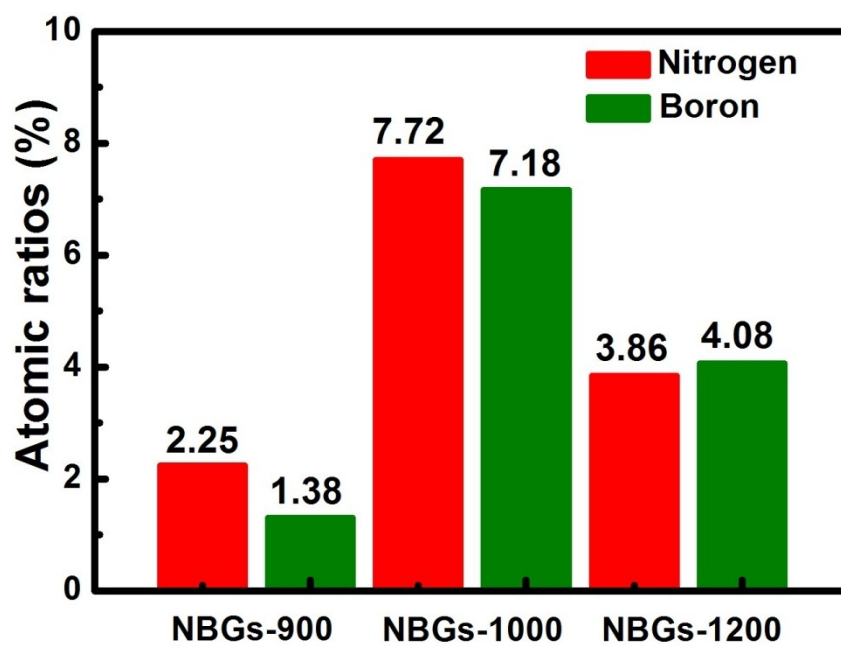


Fig. S1 Surface atomic ratios of NBGs-900, NBGs-1000 and NBGs-1200.

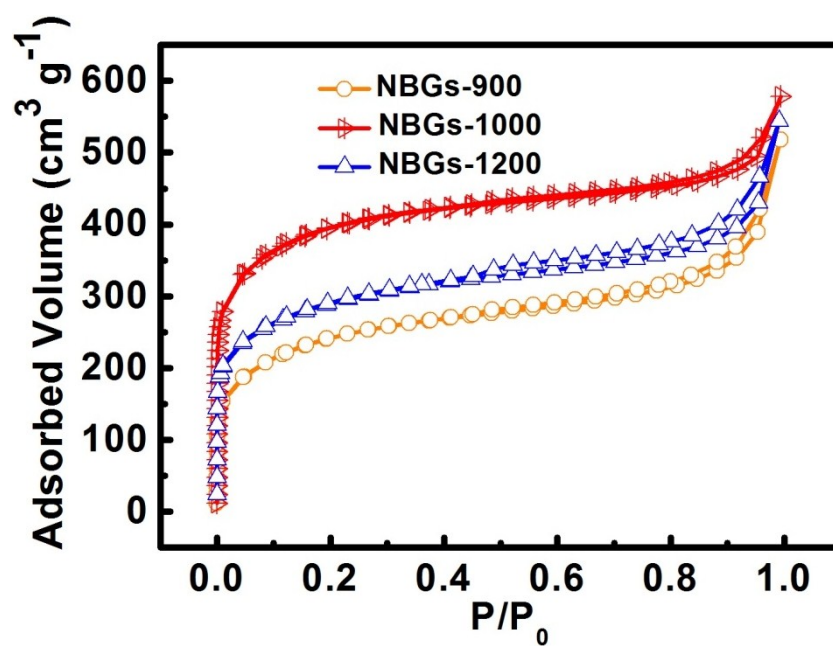


Fig. S2 N_2 adsorption/desorption isotherms of NBGs.

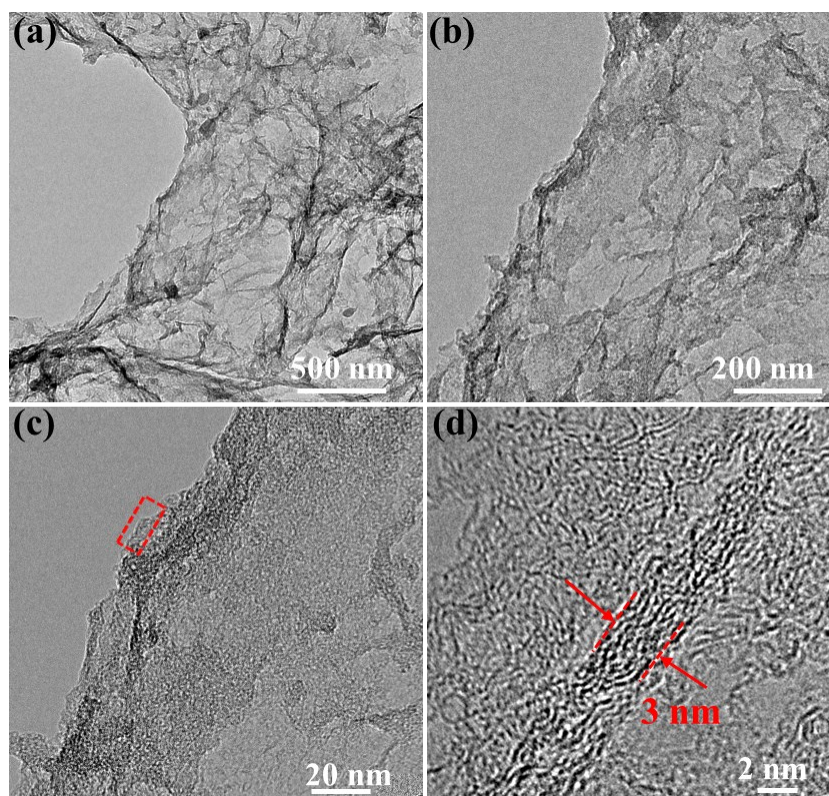


Fig. S3 (a-c) TEM images, and (d) HRTEM image of NBGs-900.

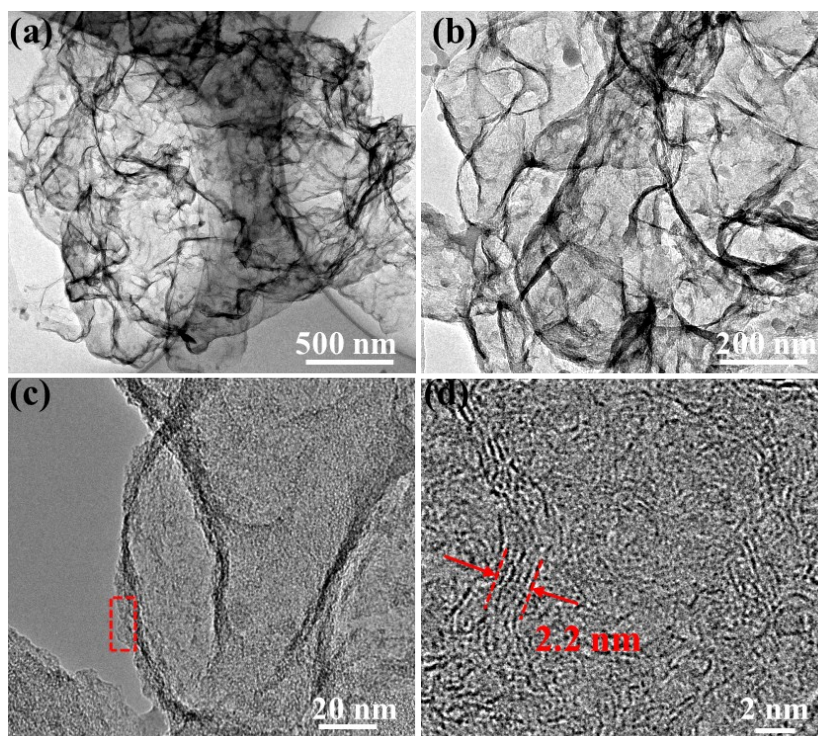


Fig. S4 (a-c) TEM images, and (d) HRTEM image of NBGs-1200.

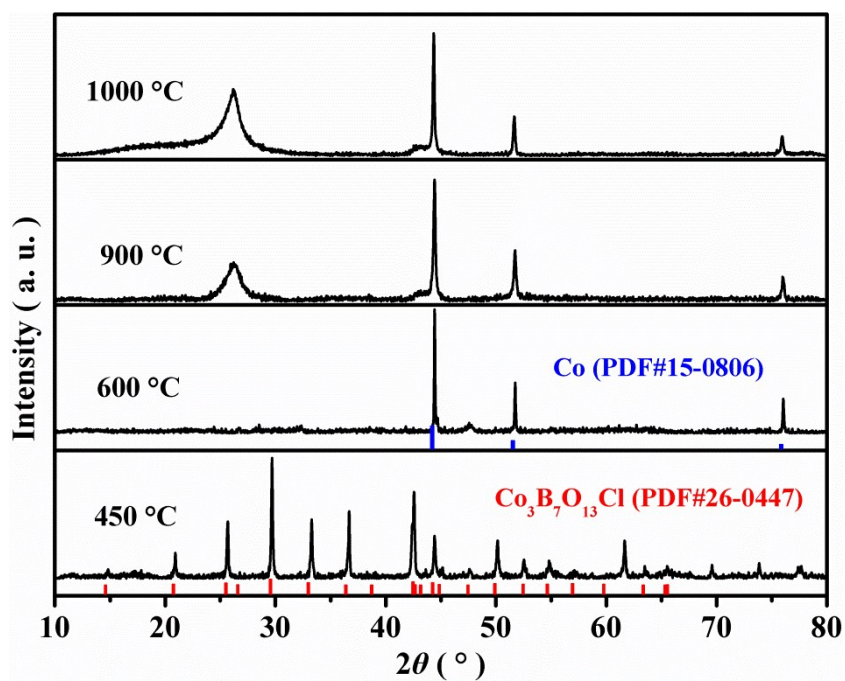


Fig. S5 XRD patterns of NBGs at different temperatures.

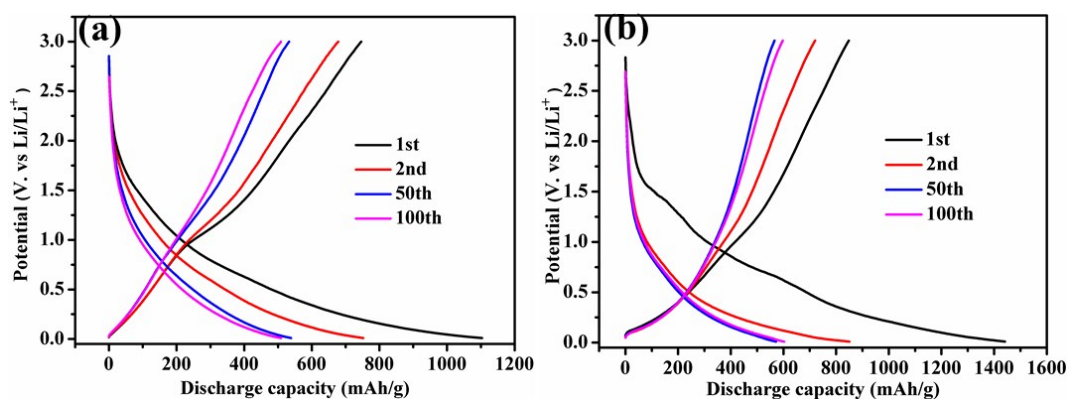


Fig. S6 Voltage profiles of NBGs-900 and NBGs-1000 at a current of 0.05 A g^{-1} in a voltage range from 0.01 V to 3 V (vs Li/Li^+).

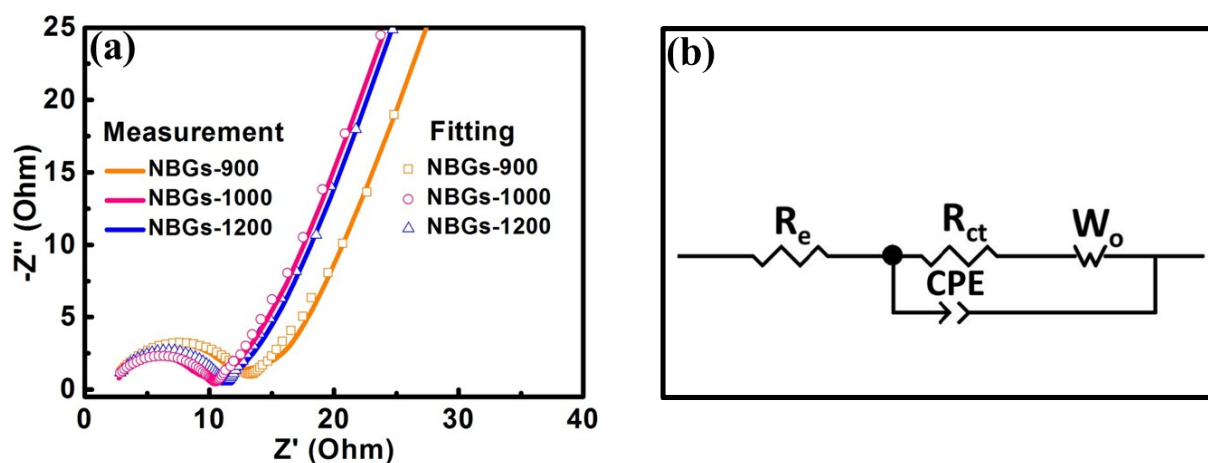


Fig. S7 (a) Electrochemical impedance spectroscopies (EIS) of NBGs and (b) equivalent circuit: R_e , R_{ct} , CPE and W_o corresponding to the resistances of electrolyte, charge transfer resistance at the electrode/electrolyte interface, constant phase element impedance and warburg impedance.

Before cycling, electrolyte resistances (R_e) of NBGs-900, NBGs-1000, and NBGs-1200 are 2.6, 2.2 and 3 Ω . Charge-transfer resistances (R_{ct}) of NBGs-900, NBGs-1000, and NBGs-1200 are 12.5, 8.9 and 10.3 Ω , respectively.

Table S1. Comparison of heteroatomic doping levels of NBGs–1000 and other representative graphene-based materials

Graphene-based materials	Doping atoms	Doping methods	Doping levels (at.%)	Ref.
Nitrogen-doped graphene	Nitrogen	Hydrothermal method with ammonium tungstate	2.85	[1]
Boron-doped graphene	Boron	CVD with phenylboronic	1.5	[2]
Phosphorus-doped graphene	Phosphorus	Thermal annealing using triphenylphosphine	1.81	[3]
Doped graphene sheets	Nitrogen	Heat treatment	3.06	[4]
	Boron	in NH_3 and BCl_3	0.88	
Nitrogen and sulfur codoped graphene	Nitrogen	Thermal treatment with	1.76	[5]
	Sulfur	2-aminothiophenol	0.86	
Nitrogen and boron co-doped graphene	Nitrogen	Hydrothermal reaction with NH_3BF_3	3.0	[6]
	Boron		0.6	
Nitrogen and fluorine dual-doped mesoporous graphene	Nitrogen	Thermal treatment of GO/ PANI	1.96	[7]
	Fluorine	and NH_4F	0.13	
Phosphorus and nitrogen dual-doped graphene sheets	Nitrogen	CVD using $(\text{NH}_4)_3\text{PO}_4$	2.6	[8]
	Phosphorus		0.6	
NBGs–1000	Nitrogen	Self-doping by borane-	7.72	This work
	Boron	tert-butylamine	7.18	

Table S2. The performances of NBGs-1000 and some representative graphene-based anode materials

Materials	Discharge current (mA g ⁻¹)	Capacity (mAh g ⁻¹)		Decay rate of per cycle	Ref.
Nitrogen and fluorine co-doped graphene	100	1073 (2nd cycle)	765 (50th cycle)	0.57%	[9]
Graphene sheets	74.4	887 (2nd cycle)	730 (200th cycle)	0.088%	[10]
Porous graphene films	50	1062 (2nd cycle)	715 (50th cycle)	0.65%	[11]
Graphene hollow spheres	100	824 (2nd cycle)	760 (100th cycle)	0.077%	[12]
Graphene/N-doped carbon	100	1100 (2nd cycle)	669 (200th cycle)	0.195%	[13]
Nitrogen-doped graphene nanosheets	100	454 (2nd cycle)	452 (100th cycle)	0.004%	[14]
Graphene sheets	50	848 (2nd cycle)	741 (50th cycle)	0.25%	[15]
Nitrogen-self-doped graphene	50	1177 (2nd cycle)	682 (95th cycle)	0.44%	[16]
Nitrogen-doped graphene	100	950 (2nd cycle)	600 (50th cycle)	0.73%	[17]
Sulfur/nitrogen dual-doped porous graphene	50	780 (2nd cycle)	440 (100th cycle)	0.43%	[18]
NBGs-1000	50	909 (2nd cycle)	877 (125th cycle)	0.028%	This work

References

- 1 X. Gu, F. Wu, B. Lei, J. Wang, Z. Chen, K. Xie, Y. Song, D. Sun, L. Sun, H. Zhou, F. Fang, *J. Power Sources*, 2016, **320**, 231-238.
- 2 H. Wang, Y. Zhou, D. Wu, L. Liao, S. Zhao, H. Peng and Z. Liu, *Small*, 2013, **9**, 1316-1320.
- 3 C. Zhang, N. Mahmood, H. Yin, F. Liu and Y. Hou, *Adv. Mater.*, 2013, **25**, 4932-4937.
- 4 Z. S. Wu, W. Ren, Li Xu, F. Li and H. M. Cheng, *ACS Nano*, 2011, **5**, 5463-5471.
- 5 W. Ai, Z. Luo, J. Jiang, J. Zhu, Z. Du, Z. Fan, L. Xie, H. Zhang, W. Huang and

- T. Yu, *Adv. Mater.*, 2014, **26**, 6186-6192.
- 6 Z. S. Wu, A. Winter, L. Chen, Y. Sun, A. Turchanin, X. Feng and K. Mullen, *Adv. Mater.*, 2012, **24**, 5130-5135.
- 7 S. Jiang, Y. Sun, H. Dai, J. Hu, P. Ni, Y. Wang, Z. Lia and Z. Li, *Nanoscale*, 2015, **7**, 10584-10589
- 8 X. Ma, G. Ning, C. Qi, C. Xu and J. Gao, *ACS Appl. Mater. Interfaces*, 2014, **6**, 14415-14422.
- 9 S. Huang, Y. Li, Y. Feng, H. An, P. Long, C. Qin and W. Feng, *J. Mater. Chem. A*, 2015, **3**, 23095-23105
- 10 S. Chen, P. Bao, L. Xiao, G. Wang, *Carbon*, 2013, **64**, 158-169.
- 11 X. Zhang, J. Zhou, C. Liu, X. Chen and H. Song, *J. Mater. Chem. A*, 2016, **4**, 8837-8843
- 12 D. Cai, L. Ding, S. Wang, Z. Li, M. Zhu and H. Wang, *Electrochim. Acta*, 2014, **139**, 96-103.
- 13 X. Liu, J. Zhang and S. G. a. N. Pinna, *J. Mater. Chem. A*, 2016, **4**, 1423-1431.
- 14 X. Li, D. Geng, Y. Zhang, X. Meng, R. Li and X. Sun, *Electrochem. Commun.*, 2011, **13**, 822-825.
- 15 D. Cai, S. Wang, P. Lian, X. Zhu, D. Li, W. Yang and H. Wang, *Electrochim. Acta*, 2013, **90**, 492-497.
- 16 C. He, R. Wang, H. Fu and P. K. Shen, *J. Mater. Chem. A*, 2013, **1**, 14586-14591.
- 17 Z. Xing, Z. Ju, Y. Zhao, J. Wan, Y. Zhu, Y. Qiang, Y. Qian, *Sci. Rep.*, **6**, 26146.
- 18 H. Shan, X. Lia, Y. Cui, D. Xiong, B. Yan, D. Li, A. Lushingtond, X. Sun, *Electrochim. Acta*, 2016, **205**, 188-197.