## **Supporting Information**

## B, N-co-doped graphene supported sulfur for superior stable Li-S half cell and Ge-S full battery

Wenlong Cai<sup>a</sup>, Jianbin Zhou<sup>a</sup>, Gaoran Li<sup>b</sup>, Kailong Zhang<sup>a</sup>, Xianyu Liu<sup>a</sup>, Can Wang<sup>b</sup>, Heng Zhou<sup>b</sup>, Yongchun Zhu<sup>\*a</sup> and Yitai Qian<sup>\*a</sup>

<sup>a</sup> Hefei National Laboratory for Physical Science at Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, 230026, P.R. China. Tel: +86-551-63601589; E-mail: ychzhu@ustc.edu.cn; Tel: +86-551-63607234; E-mail: ytqian@ustc.edu.cn

<sup>b</sup> Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China.

\*Corresponding author. Tel.: 86-551-6360-1589; Fax: +86-551-6360-0006. E-mail address: ychuzhu@ustc.edu.cn (Y. C. Zhu), ytqian@ustc.edu.cn. (Y. T. Qian)

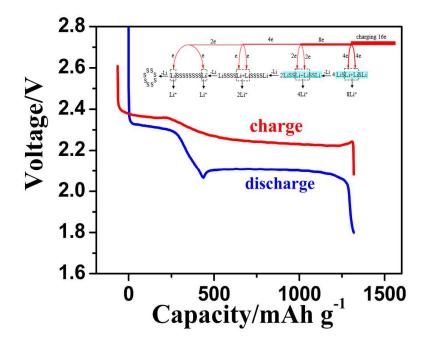


Fig. S1 Voltage profile of the S@BNG composite at the rate of 0.2 C.

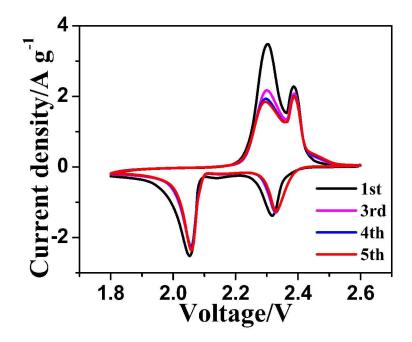


Fig. S2 The cyclic voltammetry curve of the S@BNG composite at the rate of 0.1 mV s<sup>-1</sup> in the potential range of 1.8-2.6 V.

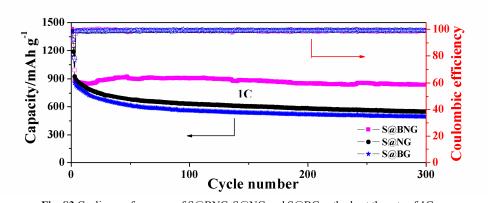


Fig. S3 Cycling performance of S@BNG, S@NG and S@BG cathode at the rate of 1C.

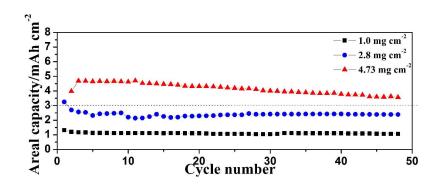


Fig. S4 Cycling performance of the S@BNG composite with different sulfur loading of 1.0, 2.8 and 4.73 mg cm<sup>-2</sup>.

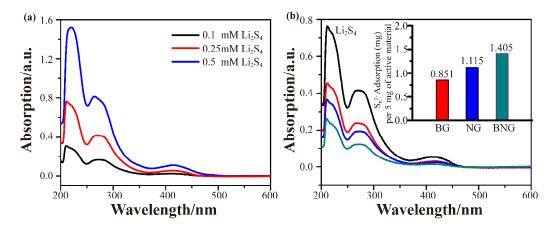


Fig.S5 (a) UV spectrum of different concentration  $Li_2S_4$  solution, (b) UV spectrum of 0.25 mM  $Li_2S_4$  and  $BG@Li_2S_4$  NG@Li\_2S\_4 and BNG@Li\_2S\_4 after 24h and the quantitative adsorption data of BG, NG and BNG respectively (inset).

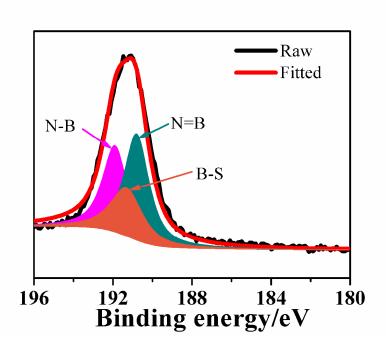


Fig.S6 N1s XPS spectra of BNG after adsorption.

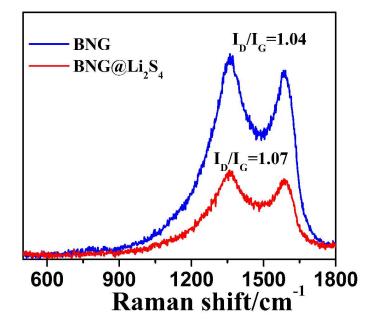


Fig. S7 Raman spectra of BNG and processed BNG@Li<sub>2</sub>S<sub>4</sub>.

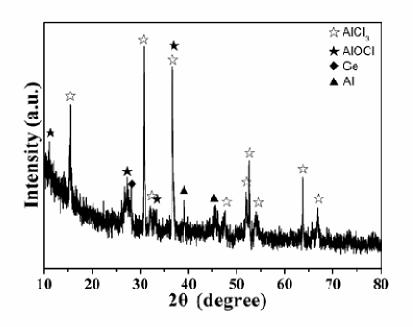


Fig. S8 The XRD pattern of crude products without any further acid treatment after reaction.

The crude products after reaction were examined by XRD to prove the reaction process. The XRD patterns can be assigned to a mixture of AlCl3 (labeled as" $\star$ " JCPDS No. 77-0819), AlOCl (labeled as" $\star$ " JCPDS No. 16-0448) and Al (labeled as " $\star$ ", JCPDS No. 01-1176) and Ge (labeled as" $\star$ "). Hence, it is reasonable to speculate that the reaction can be described as following equation:

 $4\mathrm{Al} + 3\mathrm{GeO}_2 + 2\mathrm{AlCl}_3 \rightarrow 3\mathrm{Ge} + 6\mathrm{AlOCl}$ 

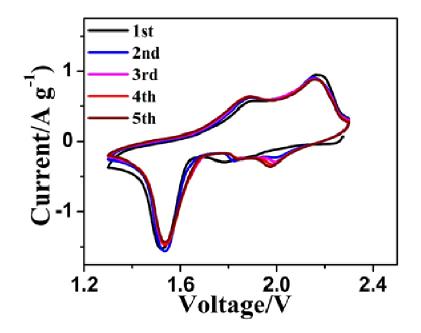


Fig. S9 The cyclic voltammetry curve of the Ge-S full battery at the rate of 0.1 mv s<sup>-1</sup> in the potential range of

1.3-2.3 V.

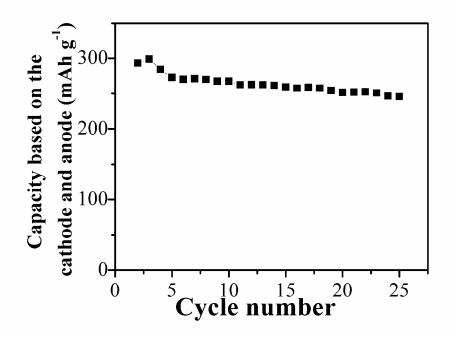


Fig.S10 Cycling performance of full lithiated Ge-S battery at the rate of 0.2 C.

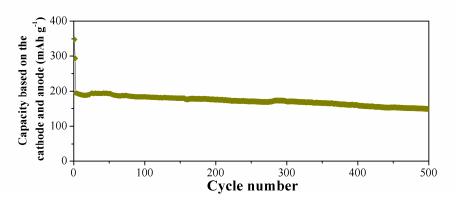


Fig.S11 Cycling performance of full lithiated Ge-S battery at the rate of 1 C.

Year	Cathode	Anode	Electrolyte	Performance	Ref.
2013	S/C	Si/C	Ionic liquid	670 mA h $g^{-1}s$ after 50 cycles at 0.1 C	[1]
2012	S/C	Si film	2% LiNO <sub>3</sub>	380 mA h $g^{-1}{}_{S}$ after 60 cycles at 0.2 C	[2]
2015	S/C	graphite	5 M Litfsi/dol	622 mA h g <sup>-1</sup> <sub>s</sub> after 100 cycles at 1 C	[3]
2015	S/C	Hard carbon	With polysulfide additive	591 mA h g $^{-1}$ s after 200 cycles at 1 C	[4]
2014	S/C	Si/C	0.25 M LiNO <sub>3</sub>	700 mA h $g^{-1}s$ after 70 cycles at 0.5 C	[5]
2015	S/C	$Li_{22}Sn_5$	Ionic liquid	an initial discharge capacity of 830 mA h $\mathrm{g}^{\text{-1}}\mathrm{_S}$	[6]
2014	S/C+ Interlayer	Carbon coated mesoporous Si	1 M Litfsi/dol	780 mA h $g^{-1}s$ after 100 cycles at 0.5 C	[7]
2015	S/C	Si/SiO <sub>x</sub> nanosphere	0.05M Li <sub>2</sub> S <sub>8</sub> 0.4M LiNO <sub>3</sub>	Over 600 mA h $g^{-1}$ <sub>s</sub> after 500 cycles at 1 C	[8]
2016	S/C	Nafion coating on Si–C	1 M Li <sub>2</sub> S <sub>4</sub>	610 mA h g <sup>-1</sup> s after 100 cycles at 0.1 C	[9]
This work	S/BNG	Nano Ge	1 M Litfsi/dol	530 mA h g <sup>-1</sup> s at 1 C over 500 cycles.	

 Table S1. Comparison of the previously reported S full batteries.

- Yan, Y.; Yin, Y.; Xin, S.; Su, J.; Guo, Y.; Wan, L. High-Safety Lithium-Sulfur Battery with Prelithiated Si/C Anode and Ionic Liquid Electrolyte. *Electrochim. Acta.* 2013, *91*, 58-61.
- (2) Elazari, R.; Salitra, G.; Gershinsky, G.; Garsuch, A.; Panchenko, A.; Aurbach, D. Rechargeable Lithiated Silicon–Sulfur (SLS) Battery Prototypes. *Electrochem. Commun.* 2012, 14, 21-24.
- (3) Lv, D.; Yan, P.; Shao, Y.; Li, Q.; Ferrara. S.; Pan, H.; Graff. G.; Polzin. B.; Wang, C.; Zhang, J.; Liu, J.; Xiao, J. High Performance Li-Ion Sulfur Batteries Enabled by Intercalation Chemistry. *Chem. Commun.* 2015, *51*, 13454-13457.
- (4) Thieme. S.; Bruckner. J.; Meier. A.; Bauer. I.; Gruber. K.; Kaspar. J.; Helmer. A.; Althues. H.; Schmuck. M.; Kaskel. S. A Lithium–Sulfur Full Cell with Ultralong Cycle Life: Influence of Cathode Structure and Polysulfide Additive. J. Mater. Chem. A 2015, 3, 3808-3820.
- (5) Brückner. J.; Thieme. S.; Hille. F.; Bauer. I.; Grossmann. H.; Strubel. P.; Althues. H.; Spange. S.; Kaskel. S.; Carbon - Based Anodes for Lithium Sulfur Full Cells with High Cycle Stability. *Adv. Funct. Mater.* 2014, 24, 1284-1289.
- (6) Ikeda, K.; Terada, S.; Mandai, T.; Ueno, K.; Dokko, K.; Watanabe, M. Lithium-Tin Alloy/Sulfur Battery with a Solvate Ionic Liquid Electrolyte. *Electrochem.* 2015, *83*, 914-917.
- (7) Pu, X.; Yang, G.; Yu, C. Safe and Reliable Operation of Sulfur Batteries with Lithiated Silicon. Nano Energy 2014, 9, 318-324.
- (8) Lee. S.; Oh. S.; Park. E.; Scrosati. B.; Hassoun. J.; Park. M.; Kim. Y.; Kim. H.; Belharouak. I.; Sun. Y. Highly Cyclable Lithium–Sulfur Batteries with a Dual-Type Sulfur Cathode and a Lithiated Si/SiOx Nanosphere Anode. *Nano letters* 2015, 15, 2863-2868.

(9) Shen, C.; Ge, M.; Zhang, A.; Fang, X.; Liu, Y.; Rong, J.; Zhou, C. Silicon (Lithiated)–Sulfur Full Cells With Porous Silicon Anode Shielded by Nafion Against Polysulfides to Achieve High Capacity and Energy Density. *Nano Energy* 2016, 19, 68-77.