Supplementary Information

Construction of low-defect and highly conductive 3D graphene network to enable high-sulphur-content cathode for high performance Li–S/graphene batteries

Shijie Zhang[ab], Weidong Xiao[ab], Yongshang Zhang[ab], Kangli Liu[ab], Xiangdan Zhang[ab], Jiangtao Zhao[a], Zhuo Wang[ab], Peng Zhang*[ab], and Guosheng Shao*[ab]

[a.] *State Center for International Cooperation on Designer Low-carbon & Environmental Materials (CDLCEM), Zhengzhou University, 100 Kexue Avenue, Zhengzhou 450001, China.*

[b.] *Zhengzhou Materials Genome Institute (ZMGI), Zhongyuanzhigu, Building 2, Xingyang 450100,China*

** Corresponding author E-mail: zhangp@zzu.edu.cn; gsshao@zzu.edu.cn*

Table S1. The C/O ratios (from XPS) and D/G (from Raman) of HCG and HCG/S

Sample	C/O (Atomic %)	D/G (Raman Intensity)
HCG	24.64	0.08
HCG/S	8.99	1.13

Table S2. Comparison of impurity levels in graphene powders prepared by various methods.

Methods	C	O	N	C/O	Reference
Solvothermal RGO, air-dried	80.4 at %	15.6 at %	4 at %	5.15	*[1]*
Solvothermal RGO, annealed at 1000℃	83.2 at %	13.8 at %	3 at %	6.03	
Hydrazine RGO, air-dried	76 at %	21 at %	3 at %	3.62	
Hydrazine RGO, annealed at 1000℃	84.5 at %	13.3 at %	2.2 at %	6.36	
$NaBH_4$ /H_2O, 80℃, 1h	69.66 wt %	19.43 wt %	0.00 wt %	4.78	*[2]*
Electrochemically exfoliated in H_2SO_4 electrolyte	-	7.5 at %	-	12.3	*[3]*
Electrochemical exfoliation of graphite	-	5.5 at %	-	17.2	*[4]*
HI reduction of GO	-	-	-	11.46	*[5]*
MW irradiation of RGO	90.51 wt %	5.60 wt %	0.00 wt %	19.4	[6]
ZMGI graphene (HCG)	**96.10 at %**	**3.90 at %**	**0.00 at %**	**24.64**	**This work**

Reference of Table S2

[1] S. Dubin, S. Gilje, K. Wang, V.C. Tung, K. Cha, A.S. Hall, J. Farrar, R. Varshneya, Y. Yang, R.B. Kaner, Acs Nano 4 (2010) 3845.

[2] W. Gao, L.B. Alemany, L. Ci, P.M. Ajayan, Nature Chemistry 1 (2009) 403.

[3] K. Parvez, R. Li, S.R. Puniredd, Y. Hernandez, F. Hinkel, S. Wang, X. Feng, K. Müllen, Acs Nano 7 (2013) 3598.

[4] K. Parvez, Z.S. Wu, R. Li, X. Liu, R. Graf, X. Feng, K. Müllen, Journal of the American Chemical Society 136 (2014) 6083.

[5] I.K. Moon, J. Lee, R.S. Ruoff, H. Lee, Nature communications 1 (2010) 73.

[6] R. Liu, Y. Zhang, Z. Ning, Y. Xu, Angewandte Chemie 56 (2017) 15677.

Table S3. Deconvolution of the C 1s peak (from XPS) in HCG/S, showing areal percentage of different carbon states. The content of carbon from C-S is about the same level of the C-C type of carbon. Carbon states associated with pickup of moisture in air are trivial.

Constituent	Areal content, %
C-C (sp^2)	47.15
C-S	45.36
C=O	3.83
O=C-OH	3.66

Table S4. Electrical conductivity of graphene prepared by various methods

Methods	Conductivity (S/m)	Reference
Solvothermal RGO	374	[1]
Solvothermal RGO, annealed at 1000℃	57300	
Hydrazine RGO, air-dried	8280	
Hydrazine RGO, annealed at 1000℃	66700	
MW irradiation of RGO	53180	[2]
Electrical current induced annealing of RGO	3112	[3]
HI reduction of GO	30400	[4]
RGO annealed 1000 °C, H2, 1 h	76000	[5]
Composite of hydrothermal RGO and vanadium nitride	1150	[6]
ZMGI graphene (HCG)	**205000**	**This work**

Reference of Table S4

[1] S. Dubin, S. Gilje, K. Wang, V.C. Tung, K. Cha, A.S. Hall, J. Farrar, R. Varshneya, Y. Yang, R.B. Kaner, ACS Nano 4 (2010) 3845.

[2] R. Liu, Y. Zhang, Z. Ning, Y. Xu, Angewandte Chemie 56 (2017) 15677.

[3] Y. Chen, K. Fu, S. Zhu, L. Wei, Y. Wang, Y. Li, E. Hitz, Y. Yao, J. Dai, J. Wan, Nano Letters 16 (2016) 3616-3623.

[4] I.K. Moon, J. Lee, R.S. Ruoff, H. Lee, Nature communications 1 (2010) 73.

[5] S. Wang, P.K. Ang, Z. Wang, A.L.L. Tang, J.T.L. Thong, K.P. Loh, Nano Letters 10 (2010) 92-98.
[6] S. Z, Z. J, Y. L, H. G, F. R, C. HM, L. F, Nature Communications 8 (2017) 14627.

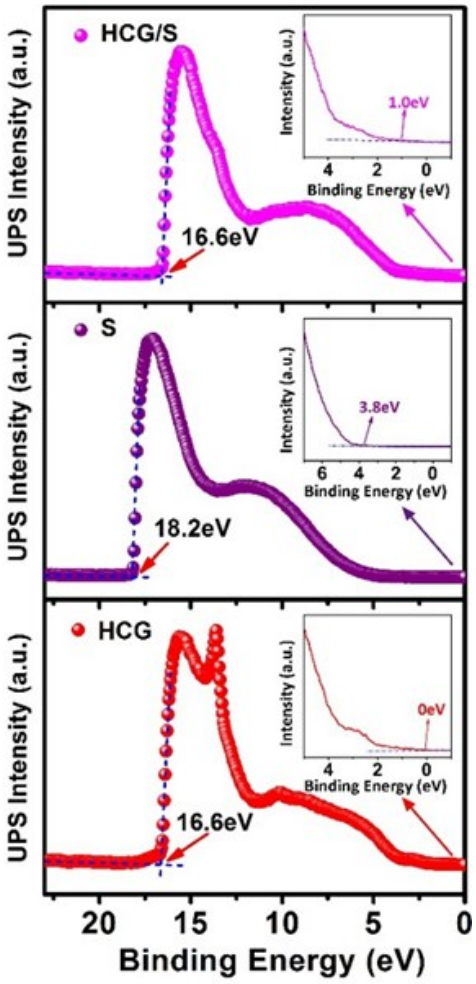

Fig. S1 UPS spectra of HCG, S and HCG/S.

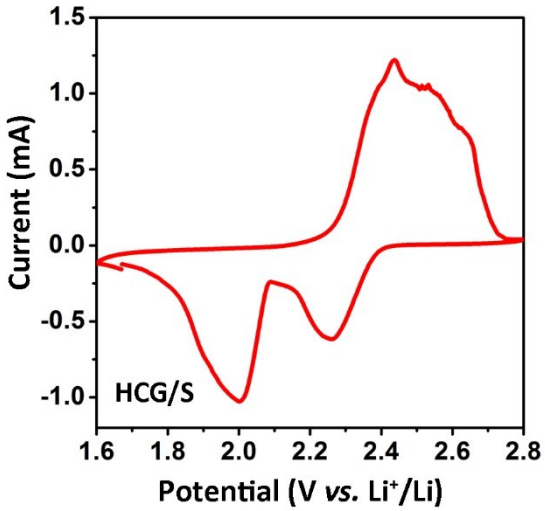

Fig. S2 Cyclic Voltammetry curves of HCG/S cathode for initial cycle.

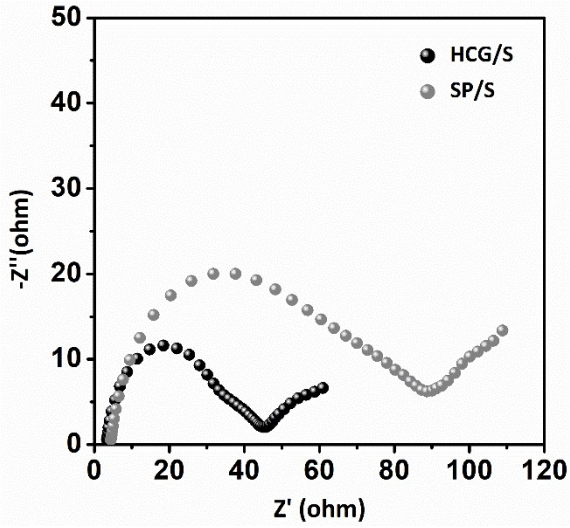

Fig. S3 Electrochemical impedance spectroscopy curves of HCG/S and SP/S cathode.

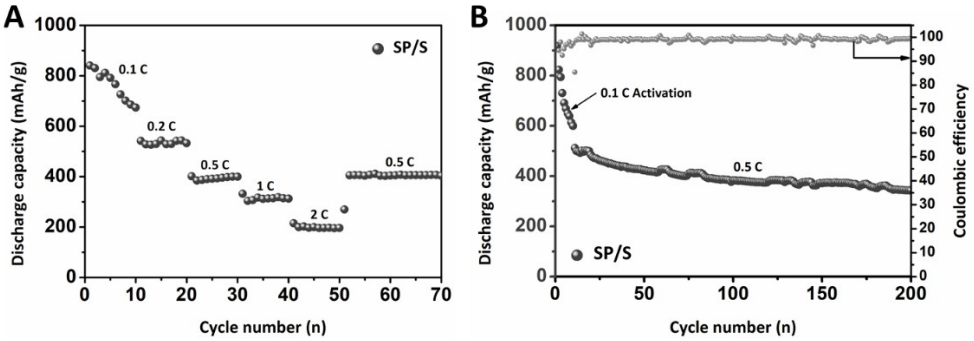

Fig. S4 (A). Rate performance of SP/S from 0.1 C to 2 C rates. (B) Cycling performances of SP/S at 0.5 C.

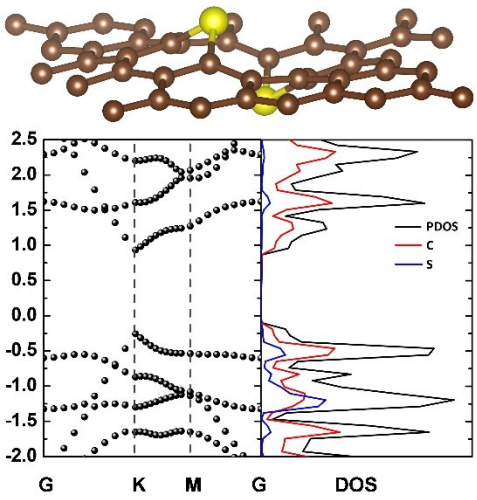

Fig. S5 Top view of optimized configurations for the two S atoms on graphene (with two consecutive point defects) substrates and associated electronic band structures; Brown, and yellow balls represent C, S, respectively.

Material parameters used for full cell energy densities:

Cathode	LFP	HCG/S	Note
Materials components	$LiFePO_4$	HCG/S (88.5 wt% S)	1. Parameters of LFP and graphite refer to the commercial pouch cells of most companies, and parameters of HCG/S is measured by present work. 2. Actual specific capacity of Li metal is considered as to be half of its total capacity. 3. The parameters of current collector, separator, and electrolyte are based on general types of the commercial products from the most companies. 4. For the calculation of the full energy density, the amount of anode is based on the match capacity of 1.2 times as cathode. 5. For the calculation of the full energy density, the volume of electrolyte is to fill all empty space in the batteries. 6. For the calculation of the full energy density, the cathode materials, anode materials, current collectors, separator and electrolyte which are the main ingredients of cells are considered. The minor factors such as mass of binder, conductive agent, electrode lugs and packing material and so on arer not considered. 7. Full energy density is based on (voltage x capacity)/ (Full mass).
Actual specific capacity (mAh/g)	140	740	
Average discharge voltage (V)	3.4	2.1	
The compacted density of cathode (g/cm^3)	2.2	1.0	
Porosity percentage of cathode (%)	39	57	
Areal loading (mg/cm^2)	30	6	
Areal density of cathode current collector (mg/cm^2)	5	5	
Anode	Graphite	Li metal	
Actual specific capacity (mAh/g)	330	1900 mAh/g	
Porosity percentage of anode (%)	33	----------	
The compacted density of anode (g/cm^3)	1.5	----------	
Areal density of anode current collector (mg/cm^2)	9	----------	
Separator thickness (μm)	25	25	
Area density of separator (mg/cm^2)	1.2	1.2	
Density of electrolyte (g/cm^3)	1.1	1.1	
Full cell density (Wh/kg)	200	660	

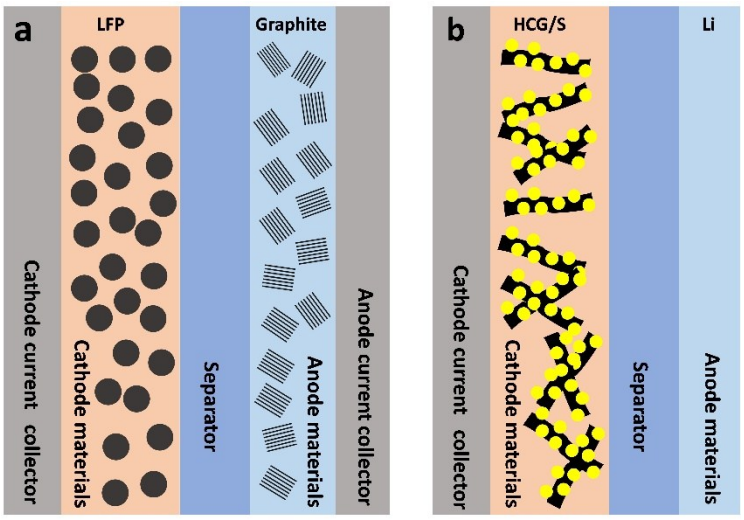

Fig. S6 Schematic diagrams for full cells: (a) LFP cell; (b) HCG/S-Li cell.