

Supplementary Information

A Novel Strategy for the Synthesis of Hard Carbon Spheres Encapsulated with Graphene Networks as a Low-Cost and Large-Scalable Anode Material for Fast Sodium Storage with an Ultralong Cycle Life

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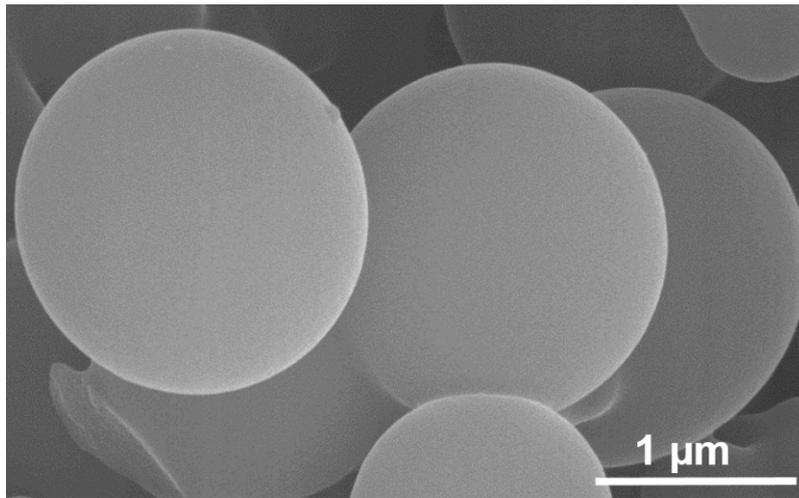


Fig. S1. SEM image of hard carbon spheres.

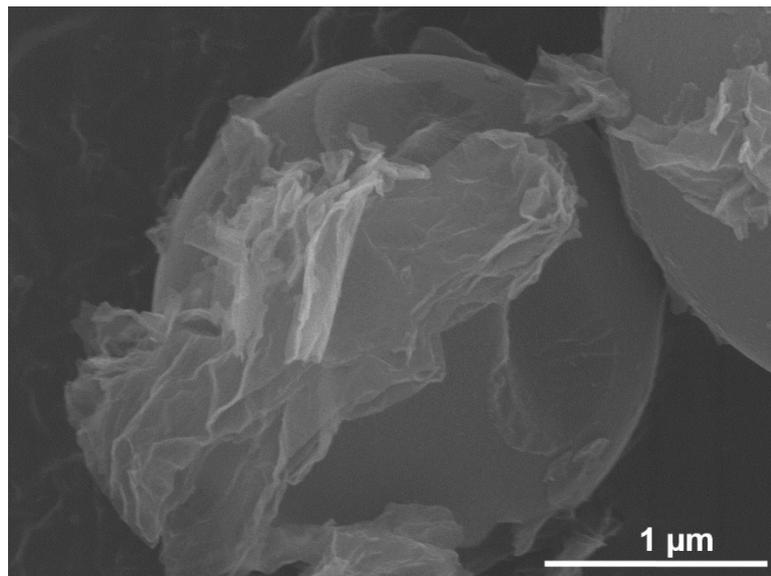


Fig. S2. SEM image of hard carbon spheres wrapped with flexible conductive networks of graphene nanosheets.

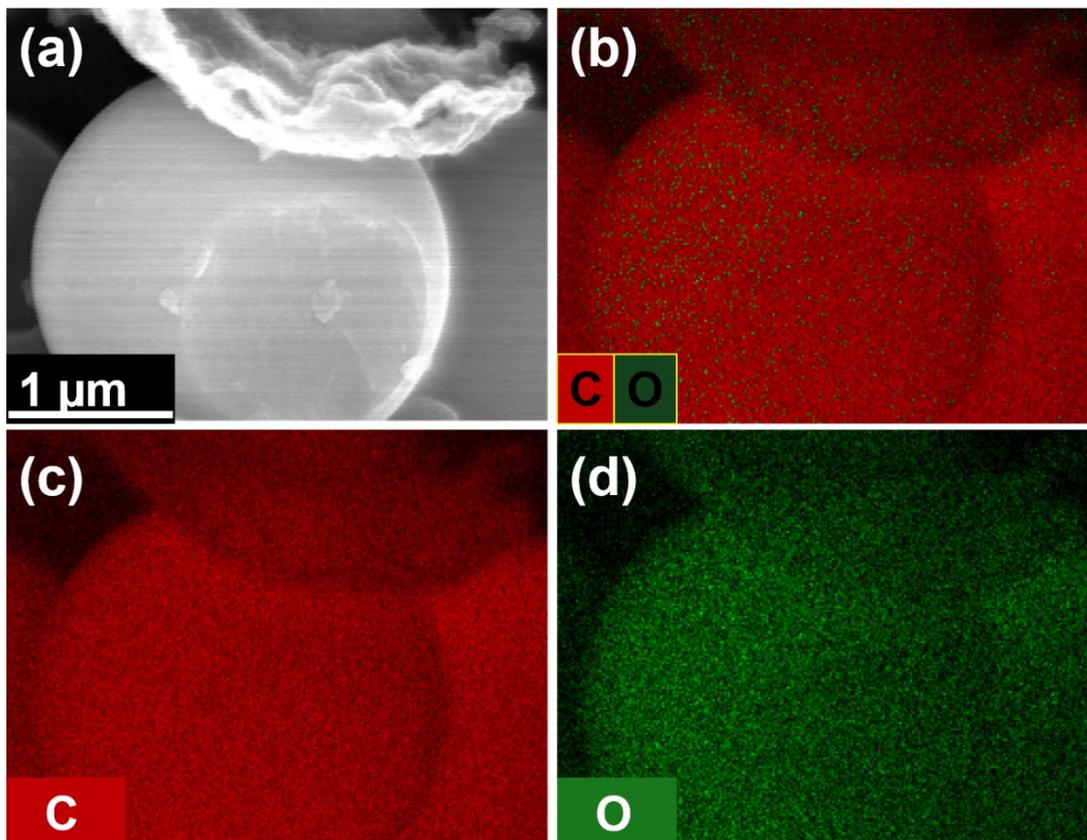


Fig. S3. SEM image (a) and (b-d) SEM-EDS elemental mapping of G-HCS.

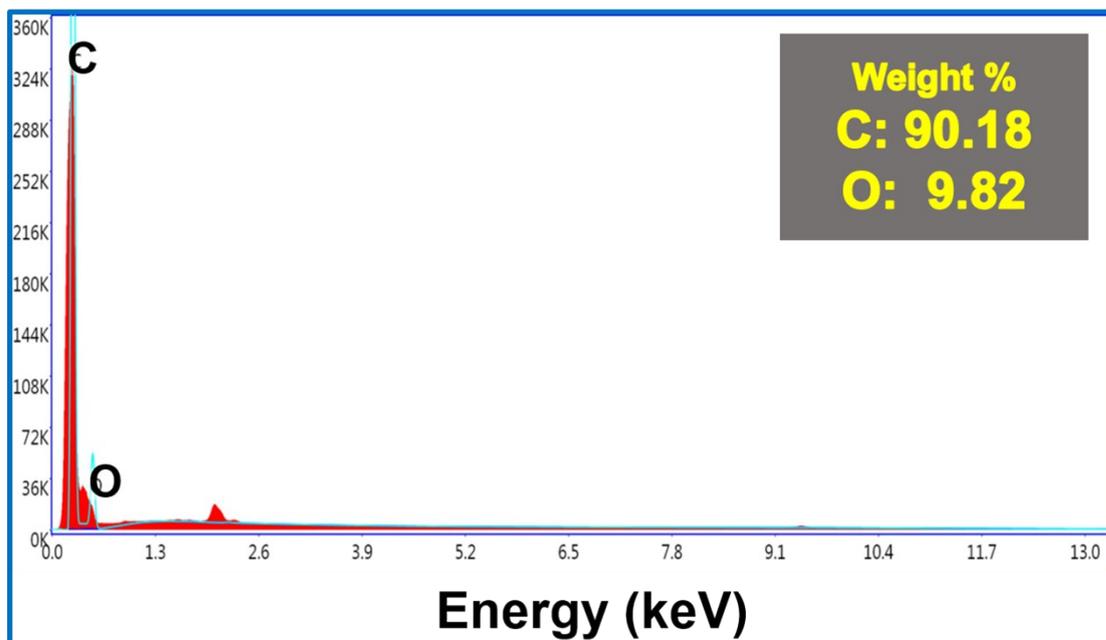


Fig. S4. EDS spectra for elemental composition of G-HCS.

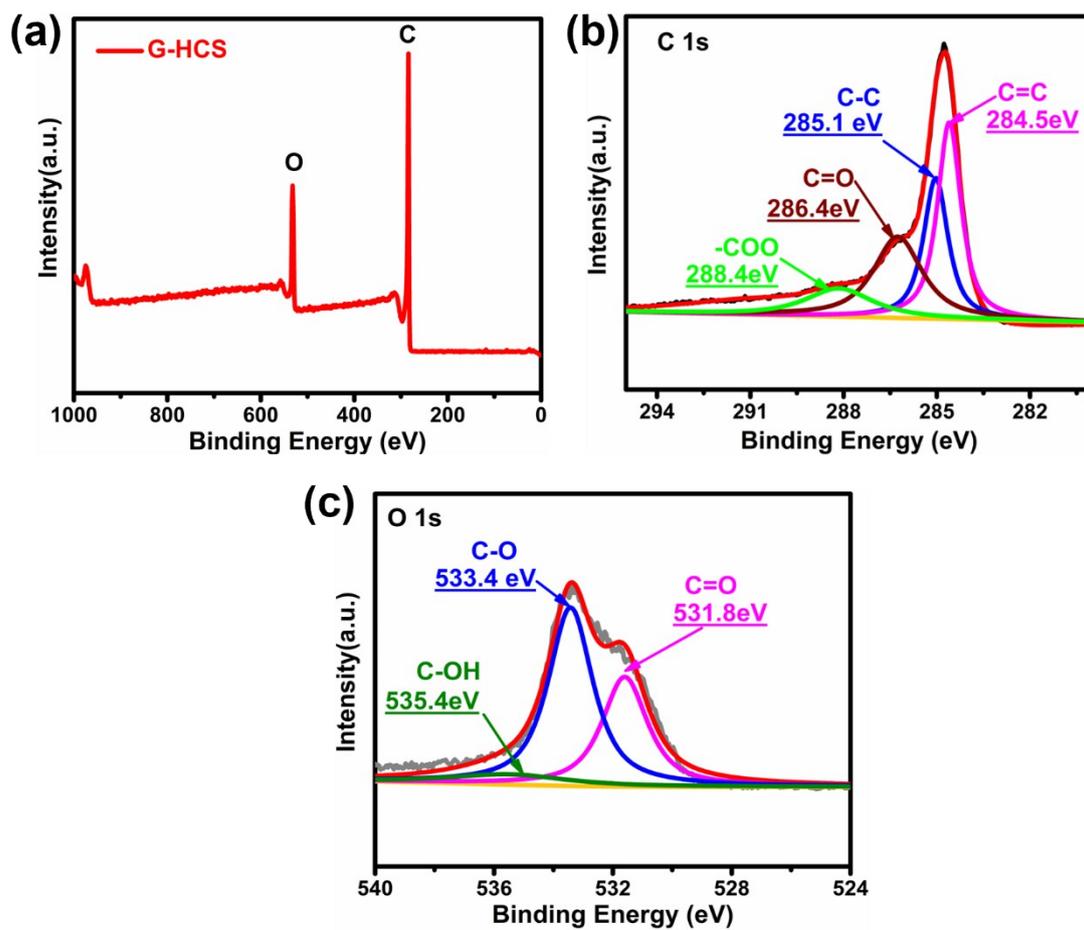


Fig. S5. XPS analysis of G-HCS sample (a) XPS survey, High-resolution XPS spectra of (b) C 1s and (c) O 1s.

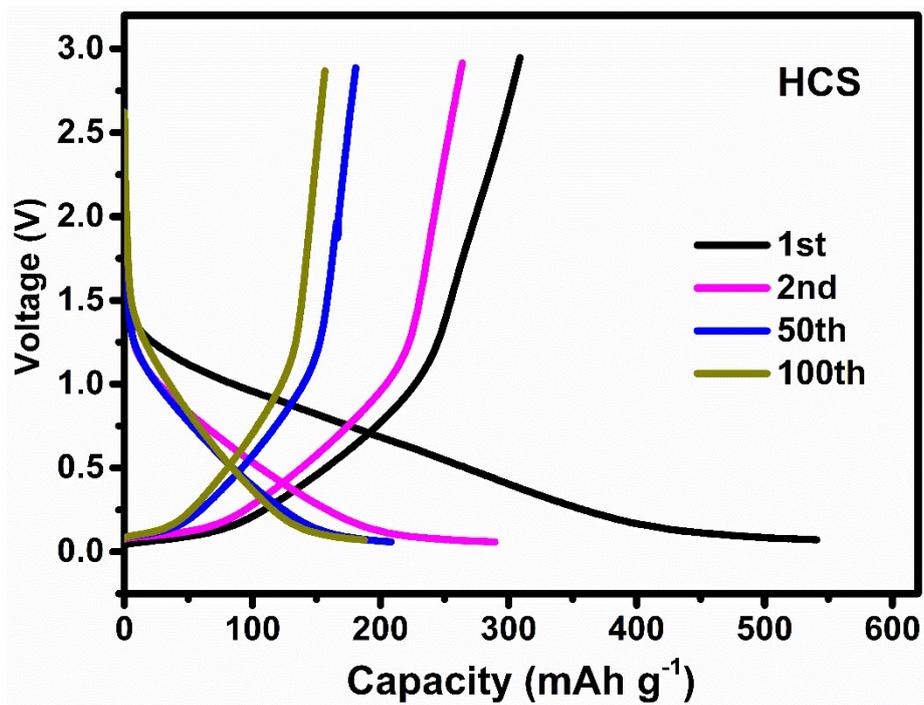


Fig. S6. Galvanostatic discharge/charge curves of HCS at current rate of 100 mA g⁻¹.

Table S1. Performance comparison of G-HCS with other reported state-of-the-art carbon anode materials for SIBs.

Carbon Anode	Initial reversible capacity (mA h g⁻¹)	Current rate for ultra-long cycling (A g⁻¹)	Cycle number	Capacity after cycles (mA h g⁻¹)	References
G-HCS	421 100 mA g⁻¹	10	4000	122	This work
Hollow Carbon Nanospheres	223 50 mA g ⁻¹	0.1	100	160	[1]
Hard Carbon Microspheres	322 28 mA g ⁻¹	0.128	40	73	[2]
Hard carbon from orange peel	220 500 mA g ⁻¹	1	1000	117	[3]
Rice husk-derived hard carbons	372 25 mA g ⁻¹	0.025	100	346	[4]
Sulfurized polyacrylonitrile derived carbon	295 500 mA g ⁻¹	10	10000	126.5	[5]
Micro-nano structure carbon	323 20 mA g ⁻¹	0.020	100	286	[6]
Carbon from Banana Peels	385 50 mA g ⁻¹	0.5	600	210	[7]
S-doped N-rich carbon	419 50 mA g ⁻¹	1	1000	211	[8]
Nitrogen-doped carbon sheets	315.2 56 mA g ⁻¹	1.69	2000	ca. 70	[9]
Amorphous carbon/graphene composite	280 100 mA g ⁻¹	0.5	2500	142	[10]
N/S codoped carbon microspheres	280 30 mA g ⁻¹	0.5	3400	ca. 150	[11]

Table S2. Performance comparison of G-HCS with other reported state-of-the-art anode materials for SIBs except carbon materials.

Carbon Anode	Initial reversible capacity (mA h g⁻¹)	Current rate for ultra-long cycling (A g⁻¹)	Cycle number	Capacity after cycles (mA h g⁻¹)	References
G-HCS	421 100 mA g⁻¹	10	4000	122	This work
Graphene-TiO₂ hybrid	265 50 mA g ⁻¹	0.5	4300	ca. 120	[12]
Amorphous SnO₂	495 50 mA g ⁻¹	1	800	220	[13]
Na₂Ti₃O₇@NDoped Carbon Hollow Spheres	297 177 mA g ⁻¹	8.8	1000	68	[14]
Graphene/Ni₂P Hybrid	516 100 mA g ⁻¹	0.3	500	161	[15]
WS₂/CNT-rGO Aerogel	305 200 mA g ⁻¹	0.2	100	252.9	[16]
Sb-C nanofibers	663 40 mA g ⁻¹	0.2	400	446	[17]
SnSe/carbon nanocomposite	447.7 500 mA g ⁻¹	0.5	200	324.6	[18]
Sb@C yolk-shell microspheres	637 50 mA g ⁻¹	0.2	200	598	[19]
Layered nickel sulfide-reduced graphene oxide composites	512.7 100 mA g ⁻¹	0.1	50	391.6	[20]

Notes and references

1. K. Tang, L. Fu, R. J. White, L. Yu, M.-M. Titirici, M. Antonietti and J. Maier, *Advanced Energy Materials*, 2012, **2**, 873-877.
2. Z. Jian, Z. Xing, C. Bommier, Z. Li and X. Ji, *Advanced Energy Materials*, 2016, **6**, 1501874.
3. J. Xiang, W. Lv, C. Mu, J. Zhao and B. Wang, *Journal of Alloys and Compounds*, 2017, **701**, 870-874.
4. Q. Wang, X. Zhu, Y. Liu, Y. Fang, X. Zhou and J. Bao, *Carbon*, 2018, **127**, 658-666.
5. J. Qian, F. Wu, Y. Ye, M. Zhang, Y. Huang, Y. Xing, W. Qu, L. Li and R. Chen, *Advanced Energy Materials*, 2018, **8**, 1703159.
6. P. Zheng, T. Liu and S. Guo, *Scientific Reports*, 2016, **6**, 35620.
7. E. M. Lotfabad, J. Ding, K. Cui, A. Kohandehghan, W. P. Kalisvaart, M. Hazelton and D. Mitlin, *ACS Nano*, 2014, **8**, 7115-7129.
8. J. Yang, X. Zhou, D. Wu, X. Zhao and Z. Zhou, *Advanced Materials*, 2017, **29**, 1604108.
9. T. Yang, T. Qian, M. Wang, X. Shen, N. Xu, Z. Sun and C. Yan, *Advanced Materials*, 2016, **28**, 539-545.
10. S. Li, J. Qiu, C. Lai, M. Ling, H. Zhao and S. Zhang, *Nano Energy*, 2015, **12**, 224-230.
11. D. Xu, C. Chen, J. Xie, B. Zhang, L. Miao, J. Cai, Y. Huang and L. Zhang, *Advanced Energy Materials*, 2016, **6**, 1501929.

12. C. Chen, Y. Wen, X. Hu, X. Ji, M. Yan, L. Mai, P. Hu, B. Shan and Y. Huang, *Nature Communications*, 2015, **6**, 6929.
13. Y. Xu, M. Zhou, C. Zhang, C. Wang, L. Liang, Y. Fang, M. Wu, L. Cheng and Y. Lei, *Nano Energy*, 2017, **38**, 304-312.
14. F. Xie, L. Zhang, D. Su, M. Jaroniec and S.-Z. Qiao, *Advanced Materials*, 2017, **29**, 1700989.
15. C. Wu, P. Kopold, P. A. van Aken, J. Maier and Y. Yu, *Advanced Materials*, 2017, **29**, 1604015.
16. Y. Wang, D. Kong, W. Shi, B. Liu, G. J. Sim, Q. Ge and H. Y. Yang, *Advanced Energy Materials*, 2016, **6**, 1601057.
17. L. Wu, X. Hu, J. Qian, F. Pei, F. Wu, R. Mao, X. Ai, H. Yang and Y. Cao, *Energy & Environmental Science*, 2014, **7**, 323-328.
18. Z. Zhang, X. Zhao and J. Li, *Electrochimica Acta*, 2015, **176**, 1296-1301.
19. J. Song, D. Xiao, H. Jia, G. Zhu, M. Engelhard, B. Xiao, S. Feng, D. Li, D. Reed, V. L. Sprenkle, Y. Lin and X. Li, *Nanoscale*, 2019, **11**, 348-355.
20. W. Qin, T. Chen, T. Lu, D. H. C. Chua and L. Pan, *Journal of Power Sources*, 2016, **302**, 202-209.