Tin Nanoparticles Embedded in Carbon Buffer Layer as Preferential Nucleation Sites for Stable Sodium Metal Anodes

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Fig. S1 (a) SEM image of tin (Sn) nanoparticles embedded in carbon network and (b) the corresponding EDS mapping of element Sn.



Fig. S2 Thermogravimetric analysis (TGA) curve of the as-prepared Sn@C composite in air at a heating rate of 5 °C min⁻¹.

Under the condition, the carbon is oxidized into gaseous CO_2 with tin oxide (SnO₂) as final product. In this case, the Sn content can be calculated according to the following equation:¹⁵





Fig. S3 SEM image of bare Sn nanoparticles on Cu foil.



Fig. S4 (a) Low-magnification and (b) high-magnification SEM images of pure carbon network without Sn nanoparticles.



Fig. S5 Coulombic efficiency of Na plating-stripping on pure carbon network without Sn nanoparticles at a current density of 2 mA cm⁻² and a capacity of 1 mAh cm⁻².



Fig. S6 Na plating curves at a current density of 2 mA cm⁻² on pure carbon matrix and Sn@C composite, respectively.



Fig. S7 Voltage profiles of Na plating-stripping at various cycles on (a) Sn@C composite; (b) bare Sn nanoparticle; (c) bare Cu foil; (d) pure carbon network at a current density of 2 mA cm⁻² and a capacity of 1 mAh cm⁻².



Fig. S8 Typical cyclic voltammetry (CV) curves (versus Na metal electrode) on bare Cu foil, bare Sn nanoparticles and Sn@C composite, respectively.



Fig. S9 Long-term voltage profiles of Na plating-stripping on different substrates at a current density and a capacity of (a) 2 mA cm⁻², 1 mAh cm⁻²; (b) 2 mA cm⁻², 3 mAh cm⁻²; (c) 2 mA cm⁻², 5 mAh cm⁻².



Fig. S10 Voltage profile of Na plating-stripping on pure carbon network without Sn nanoparticles at a current density of 2 mA cm⁻² and a capacity of 1 mAh cm⁻².



Fig. S11 (a) Low-magnification and (b) high-magnification SEM images of Na cycling at a current density 2 mA cm⁻² and a capacity of 1 mAh cm⁻² after the 50th cycle of deposition on pure carbon matrix.



Fig. S12 SEM image of commercial Na₂S cathode after grinding.



Fig. S13 Cycling performance and Coulombic efficiency of Na-S full cell using commercial Na₂S powder as cathode and Sn/Na as anode at a current rate of 1 A g^{-1} in the potential range of 1-2.6 V.



Fig. S14 Typical cyclic voltammetry (CV) curves of Na-S full cells using commercial Na₂S cathode and three kinds of anodes (Sn@C/Na, Cu/Na and Sn/Na), respectively.

NO.	Anode material	Cathode material	Current rate (A g ⁻¹)	Initial Capacity	Capacity after 100 cycles	Retention
This work	Sn@C/Na	Commercial Na ₂ S powder	1	643.7	582.3	~90.5%
1	Na metal	Nano-copper-assisted immobilizing S in high- surface-area mesoporous carbon	0.05	~700	~610	~87.1%
2	Na metal	Carbon nanotubes/Na ₂ S	0.6	~700	~380	~54.3%
3	Na metal	Activate carbon nanofibers/Na ₂ S ₆	0.3	~800	~500	~62.5%
4	Na metal	Metal organic framework-derived microporous carbon polyhedron/infusing S	0.8	860	600	~69.8%
5	Na metal	Fe nanoclusters wreathed on hollow carbon nanospheres/infusing S	0.1	1023	~500	~48.9%
6	Na metal	N-doped nanoporous carbon/infusing S	0.3	~900	~750	~83.3%
7	Na metal	Porous carbon/BaTiO $_3$ nanofibers/infusing S	1	~952	~450	~47.3%
8	Na metal	Multiporous carbon fibers/infusing S	1.6	~1450	~850	~58.6%
9	Na metal	Cobalt nanoparticles-decorated hollow carbon/infusing S	0.1	~1081	~600	~55.6%
10	Na metal	Sugar-derived carbon spheres/infusing S	1.6	~420	~310	~73.8%
11	Na metal	Carbonized polyacrylonitrile matrix/infusing S	1.6	~350	~220	~62.9%
12	Hard carbon after tailed sodiation	Porous Ketjenblack carbon/infusing S	0.167	~1000	~580	~58%
13	Passivated Na metal	Hollow Na ₂ S nanospheres embedded in a hierarchical and spongy carbon matrix	2.1	~790	~400	~50.6%
14	Na metal	Activate carbon nanofibers/Na ₂ S	0.3	580	500	~86.2%

Table S1. Comparison of cycling performance of room-temperature Na-S batteries in this work with reported literatures (based on S mass).¹⁻¹⁴

References

1. S. Zheng, P. Han, Z. Han, P. Li, H. Zhang and J. Yang. Adv. Energy Mater. 2014, 4, 1400226.

- 2. X. Yu and A. Manthiram. Chem. Eur. J. 2015, 21, 4233-4237.
- 3. X. Yu and A. Manthiram. Adv. Energy Mater. 2015, 5, 1500350.

4. S. Wei, S. Xu, A. Agrawral, S. Choudhury, Y. Lu, Z. Tu, L. Ma and L. A. Archer. *Nat. Commun.* 2016, 7, 11722.

5. B-W. Zhang, T. Sheng, Y-X. Wang, S. Chou, K. Davey, S-X. Dou and S-Z. Qiao, *Angew. Chem. Int. Ed.* 2019, **58**, 1484-1488.

6. Y-M. Chen, W. Liang, S. Li, F. Zou, S. M. Bhaway, Z. Qiang, M. Gao, B. D. Vogt and Y. Zhu. *J. Mater. Chem. A*, 2016, **4**, 12471-12478.

7. D. Ma, Y. Li, J. Yang, H. Mi, S. Luo, L. Deng, C. Yan, M. Rauf, P. Zhang, X. Sun, X. Ren, J. Li and H. Zhang. *Adv. Funct. Mater.* 2018, **28**, 1705537.

8. X. Xu, D. Zhou, X. Qin, K. Lin, F. Kang, B. Li, D. Shanmukaraj, T. Rogo, M. Armand and G. Wang. *Nat. Commun.* 2018, **9**, 3870.

B-W. Zhang, T. Sheng, Y-D. Liu, Y-X. Wang, L. Zhang, W-H. Lai, L. Wang, J. Yang, Q-F. Gu, S-L. Chou, H-K. Liu and S-X. Dou, *Nat. Commun.* 2018, 9, 4082.

10. R. Carter, L. Oakes, A. Douglas, N. Muralidharan, A. P. Cohn and C. L. Pint. *Nano Lett.* 2017, **17**, 1863-1869.

11. T. H. Hwang, D. S. Jung, J-S. Kim, B. G. Kim and J. W. Choi. *Nano Lett.* 2013, **13**, 4532-4538.

12. M. Kohl, F. Borrmann, H. Althues and S. Kaskel. Adv. Energy Mater. 2016, 6, 1502185.

13. C. Wang, H. Wang, X. Hu, E. Matios, J. Luo, Y. Zhang, X. Lu and W. Li, *Adv. Energy Mater.* 2019, **9**, 1803251.

14. X. Yu and A. Manthiram. Chem. Mater. 2016, 28, 896-905.

15. Z. Zhu, S. Wang, J. Du, Q. Jin, T. Zhang, F. Cheng and J. Chen, *Nano Lett.* 2014, 14, 153-157