Supporting Information for

## Rational Microstructure Design of SnS<sub>2</sub>-Carbon Composites for Superior Sodium Storage Performance

Yi Zhao,<sup>a</sup> Binbin Guo,<sup>a</sup> Qianqian Yao,<sup>a,b</sup> Jiaxin Li,<sup>a</sup> Jianshuo Zhang,<sup>a,b</sup> Kun Hou,<sup>a</sup> and Lunhui Guan\*<sup>a</sup>

<sup>a</sup>CAS Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350108, China. E-mail: guanlh@fjirsm.ac.cn

<sup>b</sup>University of Chinese Academy of Sciences, Beijing, 100049, China



Fig. S1 SEM images of (a) MWNT@SnO<sub>2</sub>, (b) MWNT@SnO<sub>2</sub>@C, (c) MWNT@SnO<sub>2</sub>@void@C, (d) MWNT@SnS<sub>2</sub> NS, (e) MWNT@SnS<sub>2</sub>@C, and (f) MWNT@SnS<sub>2</sub> NS@C composites.



Fig. S2 TEM images of MWNT@SnO<sub>2</sub>@SiO<sub>2</sub>@C composites. As can be seen, MWNTs were sequentially coated with SnO<sub>2</sub>, SiO<sub>2</sub>, and carbon layers.



Fig. S3 Selected area electron diffraction (SAED) patterns of (a) MWNT@SnO<sub>2</sub>@void@C, and (b) MWNT@SnS<sub>2</sub> NS@C composites, from which the diffraction rings can be well assigned to tetragonal SnO<sub>2</sub> and hexagonal SnS<sub>2</sub>, respectively.



Fig. S4 TEM images of pure  $SnS_2$  nanosheets. The hydrothermal synthesized  $SnS_2$  NS exhibited large lateral size of 400-600 nm and thickness around 90 nm. The interplanar spacing of 0.27 nm in Fig. S3d could be assigned to the (101) plane of hexagonal  $SnS_2$ .



Fig. S5 (a, c, e) XRD patterns, and (b, d, f) TGA curves of (a-b) pure SnS<sub>2</sub> NS, (c-d) MWNT@SnS<sub>2</sub> NS, and (e-f) MWNT@SnS<sub>2</sub>@C composite. The XRD patterns of these three sample were well indexed to the hexagonal SnS<sub>2</sub> (JCPDS No.23–0677). Seen from the TGA curve of pure SnS<sub>2</sub> NS in Fig. S3b, one weight loss region from 400-530 °C was resulted from the oxidation of SnS<sub>2</sub> to SnO<sub>2</sub>. The weight content of SnS<sub>2</sub> was almost 100%. In Fig. S3d, two regions at 400-500 °C and 500-690 °C were ascribed to the oxidation of SnS<sub>2</sub> and weight loss of MWNTs, respectively. The weight content of SnS<sub>2</sub> in MWNT@SnS<sub>2</sub>@C, there were three temperature regions at 390-470 °C, 470-570 °C, and 570 to 680 °C, corresponding to the formation of SnS<sub>2</sub> in MWNT@SnS<sub>2</sub>@C composite was around 57 wt%.



Fig. S6 (a, c, e) Nitrogen adsorption—desorption isotherms, and (b, d, f) pore size distribution curves of (a-b)  $SnS_2$  NS, (c-d) MWNT@SnS<sub>2</sub> NS, and (e-f) MWNT@SnS<sub>2</sub>@C composites.



Fig. S7 Selected discharge-charge profiles of (a)  $SnS_2 NS$ , (b) MWNT@SnS<sub>2</sub> NS, and (c) MWNT@SnS<sub>2</sub>@C electrodes at a current density of 100 mA g<sup>-1</sup>.

Materials	Current density (mA g <sup>-1</sup> )	Cycle Number	Capacity (mAh g <sup>-1</sup> )	Reference
Graphene-SnS <sub>2</sub> nanosheets	0.2	100	630	[1]
Graphene-SnS <sub>2</sub> nanoplates	0.02	60	670	[2]
Graphene-SnS <sub>2</sub> nanoparticles	0.05	50	610	[3]
SnS <sub>2</sub> nanosheets	0.1	50	647	[4]
Graphene-SnS <sub>2</sub>	0.2	300	509	[5]
Graphene-SnS <sub>2</sub> nanoplates	0.2	100	619	[6]
Graphene-SnS <sub>2</sub> nanocrystals	0.2	100	680	[7]
N-doped graphene-SnS <sub>2</sub> nanoparticles	0.2	100	450	[8]
Graphene-SnS <sub>2</sub>	0.1	100	826	[9]
Graphene-SnS <sub>2</sub> nanocrystals	1	100	418	[10]
Carbon nanotube-SnS <sub>2</sub> nanosheets	0.1	100	660	[11]
Carbon nanotube- $SnO_2$ - $SnS_2$	0.05	100	355	[12]
MWNT@SnS2 NS@C	0.1	100	710	Our work

Table S1. Electrochemical performance of carbon- $SnS_2$  composites as anode materials for NIBs.

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Fig. S8 High-resolution Sn  $3d_{5/2}$  XPS spectra of fresh MWNT@SnS<sub>2</sub> NS electrode. The binding energies of Sn  $3d_{5/2}$  before cycle was located at 487.1 eV, in consistent with the data for Sn  $3d_{5/2}$  in SnS<sub>2</sub>.



Fig. S9 HRTEM images of MWNT@SnS<sub>2</sub> NS@C electrode after first discharge to 0.6 V (a), after first discharge to 0.05 V (b), after first charge to 1.5 V (c), and first charge to 2.8 V (d).



Fig. S10 EIS profiles of  $SnS_2$  NS, MWNT@ $SnS_2$  NS, MWNT@ $SnS_2$ @C, and MWNT@ $SnS_2$  NS@C electrodes before cycling (a) and after 100 cycles (b).