Electronic Supplementary Information for

A robust composite of SnO_2 hollow nanospheres enwrapped by graphene as high-capacity anode materials for lithium-ion batteries

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Experimental Section

Preparation of Graphite Oxide: The graphite oxide was made from natural graphite flake (Alfa Aesar, 325 mesh) by a modified Hummers method.[1]

Preparation of SnO_2 Hollow Nanospheres: Silica nanospheres were firstly synthesized by the well-known Stöber's method.[2] 3 mL of concentrated aqueous NH_4OH, 75 mL of EtOH, and 10 mL of H_2O were mixed together by stirring. 7.2 mL of TEOS (tetraethylorthosilicate) was then added in the solution and stirred for 5 h. Afterwards, polycrystalline SnO_2 shells were formed on the surface of SiO_2 nanospheres by a modified Lou method.[3] 8.0 g of urea and 1.2 g $K_2SnO_3 \cdot 3H_2O$ was dissolved in 120 mL of DI water, and then 80 mL of EtOH was added in the solution to achieve pale milky suspension under stirring. 1.2 g of SiO_2 nanospheres were dispersed in 40 mL DI water with sonication (KQ3200DE, 40 kHz). The two suspensions were admixed for 5 min and then transferred to 4×100 mL Teflon autoclaves, which was heated at 170 ^oC for 30 h. Finally, the SiO_2 core was etched away in 2 M aqueous NaOH solution at 50 ^oC for 3-6 h to obtain SnO_2 hollow nanospheres.

Preparation of Graphene enwrapped SnO_2 Hollow Nanospheres (SnO_2-HNS/G): In a typical synthesis of SnO_2-HNS/G, 4 mL of graphite oxide aqueous suspension (10.0 mg mL^{-1}) was diluted to 1.0 mg mL^{-1} with DI water and was sonicated for 10 min to achieve a brown homogeneous graphene oxide aqueous suspension. Then, 160 mg of

SnO_2 hollow nanospheres were dispersed in 20 mL of water via 6 min sonication. Afterwards, the as-obtained SnO_2 hollow nanospheres aqueous suspension was added into the graphene oxide aqueous suspension, and the obtained mixture was sonicated for 5 min to achieve a uniform SnO_2 hollow nanospheres/graphene oxide aqueous suspension. The resulting homogeneous aqueous suspension was frozen by liquid nitrogen and lyophilized, followed by thermal reduction in a crucible in a tube furnace at 500 ^oC for 2 h under Ar atmosphere with a heating rate of 2 ^oC min^{-1} to obtain the SnO_2-HNS/G.

Structural and Electrochemical Characterizations: TEM and HRTEM analysis was performed on a Tecnai G2 F20 U-TWIN field emission transmission electron microscope operated at 200 kV. SEM measurement was carried out with a JEOL 6701 field emission scanning electron microscope operated at 10 kV. Thermogravimetric (TG) analysis was conducted on a TA-Q50 instrument. XPS analysis was performed on an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlKα radiation. XRD measurements were recorded on a Rigaku D/max2500 diffractometer using CuKα radiation. Nitrogen adsorption and desorption isotherms at 77.3 K were carried out with a Nova 2000e surface area-pore size analyzer. Electrochemical experiments were performed using Swagelok-type cells. To prepare working electrodes, SnO_2-HNS/G, Super-P carbon black, and poly(vinylidene fluoride) (PVDF) with mass ratio of 80:10:10 were mixed into a homogeneous slurry with mortar and pestle, and then the obtained slurry was pasted onto pure Cu foil (99.9 %, Goodfellow). The loading mass of active materials is about 10 mg cm^{-2}. The electrolyte was 1 M $LiPF_6$ in EC/DMC/DEC (1:1:1 v/v/v) (Tianjing Jinniu Power Sources Material Co. Ltd). Glass fibers (GF/D) from Whatman were used as separators and pure lithium metal foil (Aldrich) was used as the counter electrode. The Swagelok-type cells were assembled in an argon-filled glove box. Cyclic voltammetry was performed on a Voltalab 80 electrochemical workstation at a scan rate of 0.1 mV s^{-1}. The discharge and charge measurements of the batteries were performed on an Arbin BT2000 system in the fixed voltage window between 0.005 and 3 V at room temperature. Electrochemical impedance spectral measurements

were carried out with a PARSTAT 2273 advanced electrochemical system over the frequency range from 100 kHz to 10 mHz.

Supplementary Figures

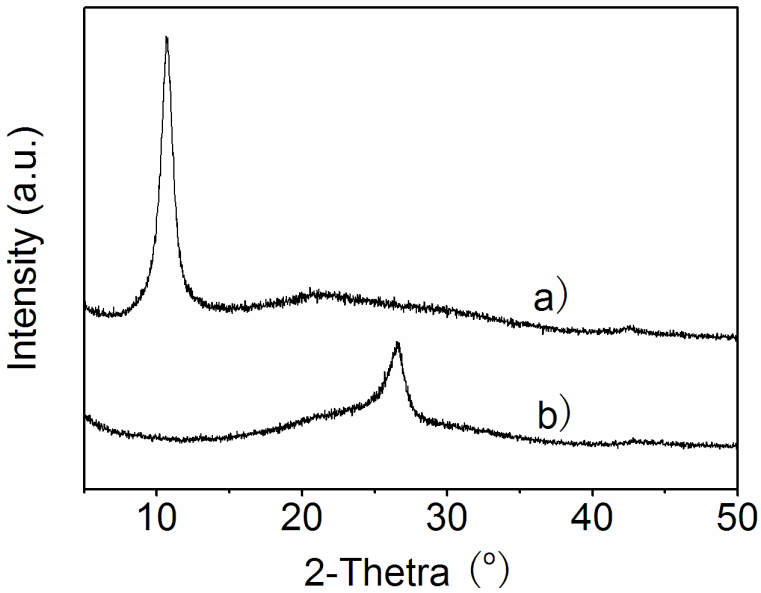

Figure S1. XRD patterns of a) graphene oxide and b) graphene sheets. The characteristic peaks in the XRD patterns of graphene oxide and graphene sheets are appeared at 10.7° and 26.4°, corresponding to the layer-to layer distance (*d*-spacing) of 0.829 nm and 0.338 nm, respectively.

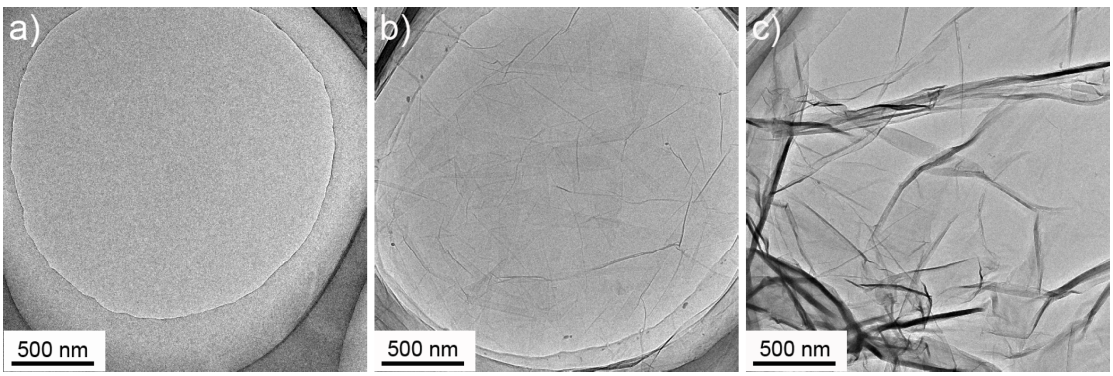

Figure S2. TEM images of a) holey carbon films, b) graphene oxide, and c) graphene sheets.

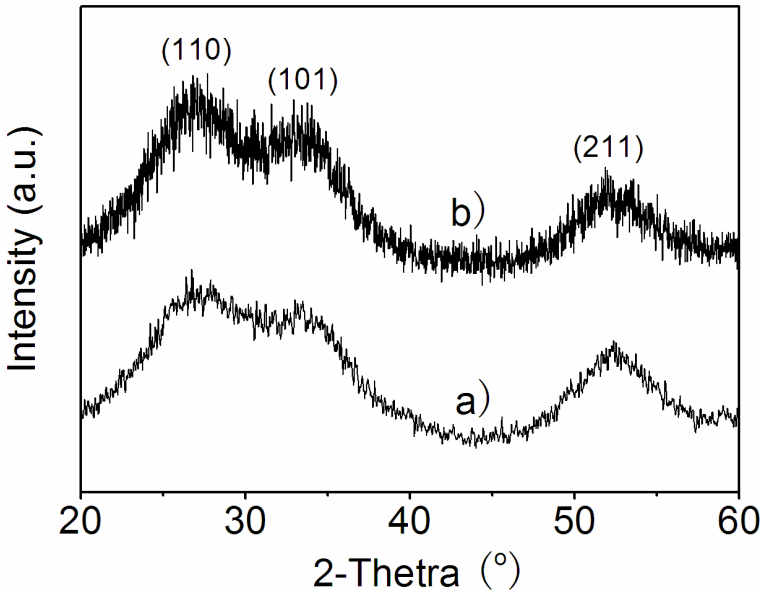

Figure S3. XRD patterns of a) SnO_2 hollow nanospheres and b) SnO_2-HNS/G.

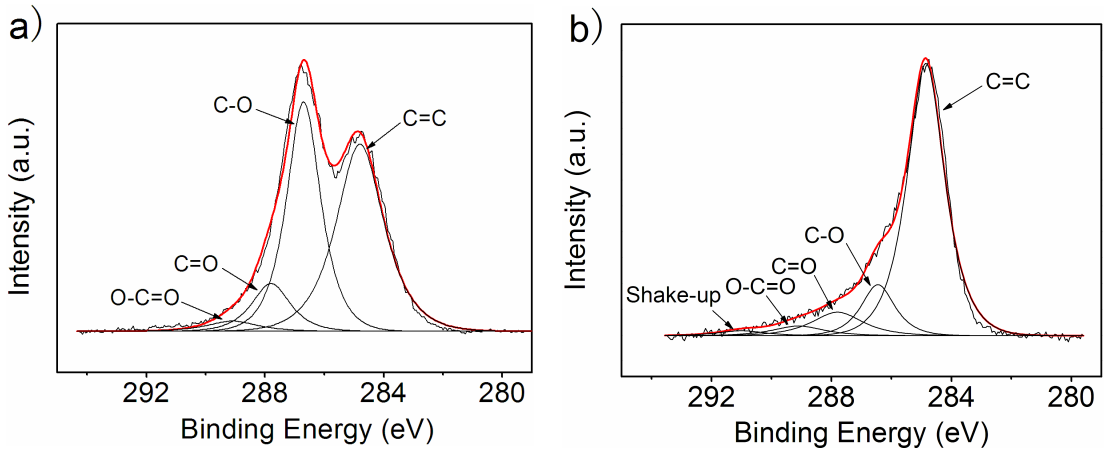

Figure S4. XPS C 1s spectra of a) GO and b) SnO_2-HNS/G.

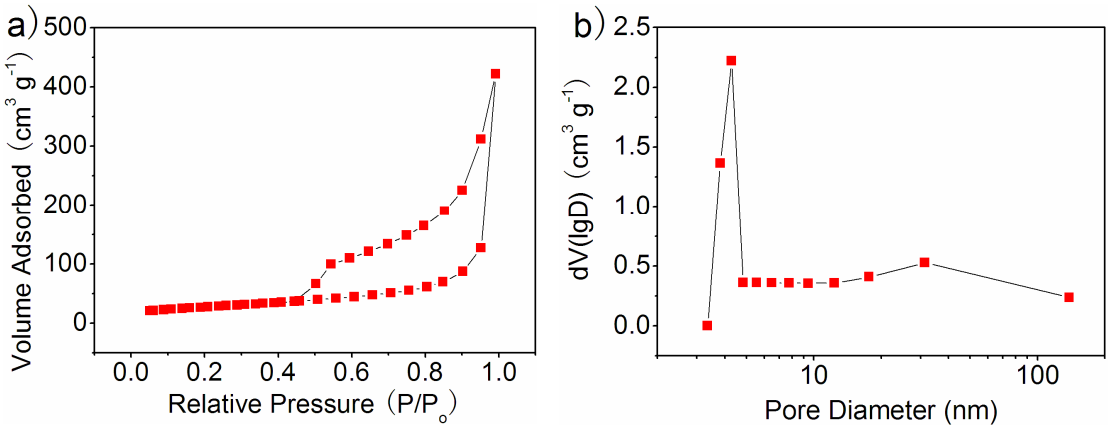

Figure S5. a) Nitrogen adsorption/desorption isotherms of the SnO_2-HNS/G, b) pore-size distribution plot calculated using the BJH formula with the desorption isotherm.

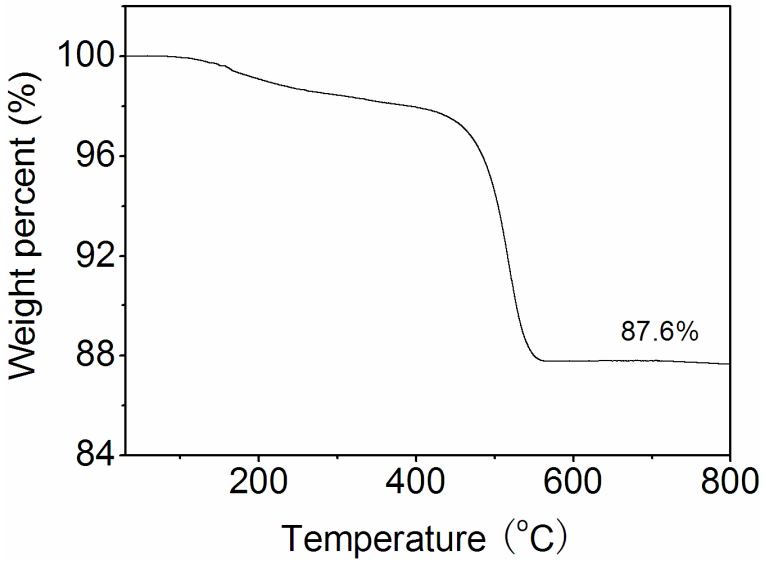

Figure S6. TG analysis curve of the SnO_2-HNS/G under air atmosphere at a heating rate of 10 ^oC min^{-1}.

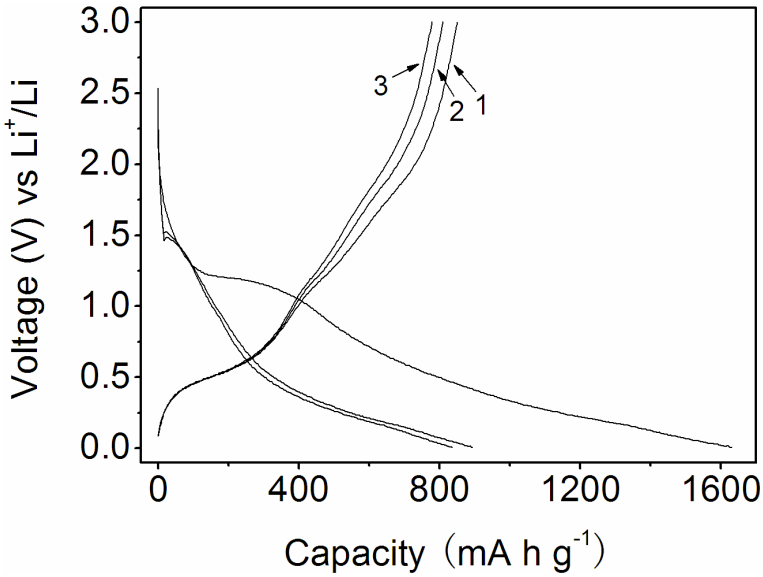

Figure S7. Galvanostatic discharge-charge profiles of the first three cycles of the SnO_2-HNS/G under a current density of 0.5 A g^{-1} within the voltage range of 0.005–3 V vs Li^+/Li.

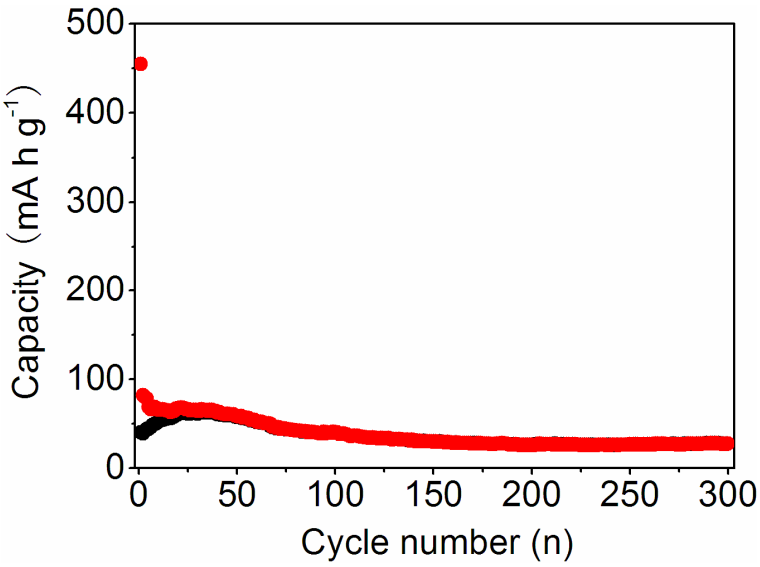

Figure S8. Cycling performance of the SnO_2 hollow nanospheres under a current density of 0.5 A g^{-1} between the voltage limits of 0.005–3 V vs Li^+/Li.

Table S1. Summary of reversible specific capacities of SnO_2/graphene composites reported previously and in present work.

Current density (mA g^{-1})	Voltage range (V) vs Li^+/Li	Initial capacity (mA h g^{-1})	Cycle number (n)	Residual capacity (mA h g^{-1})	Ref.
156	0.02–3	786	50	558	34
67	0.01–2	978	30	840	36
100	0.001–3	852	50	634	37
100	0.01–2	819	50	626	38
50	0.05–2	810	30	570	39
100	0.005–3	1000	50	775	42
100	0.01–3	936	100	1156	43
100	0.01–3	1104	200	590	44
100	0.005–1.5	690	20	433	45
500	0.005–3	850	300	696	Present work

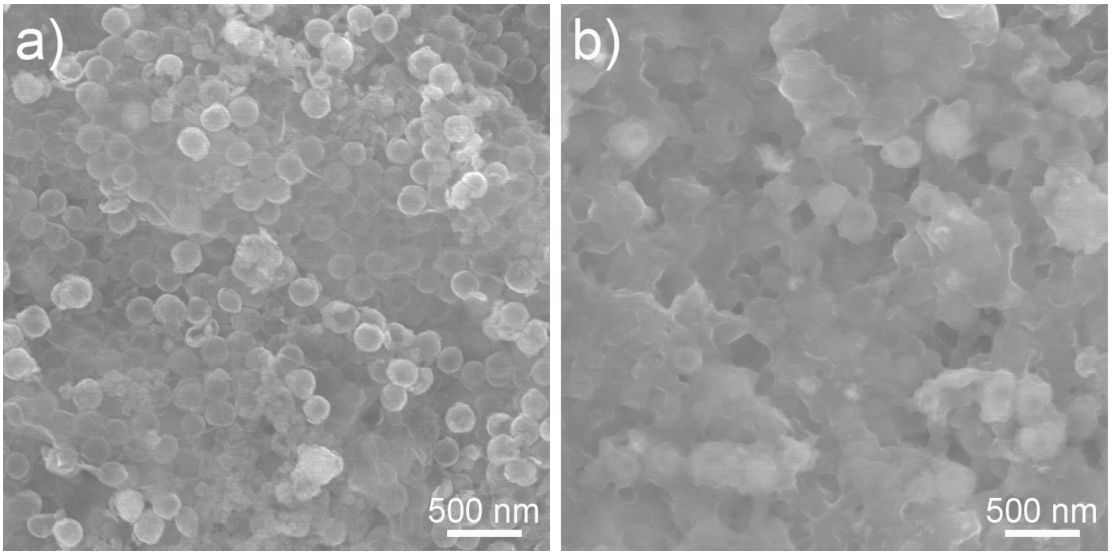

Figure S9. SEM images of the SnO_2-HNS/G electrode a) before cycling, b) after rate capability testing.

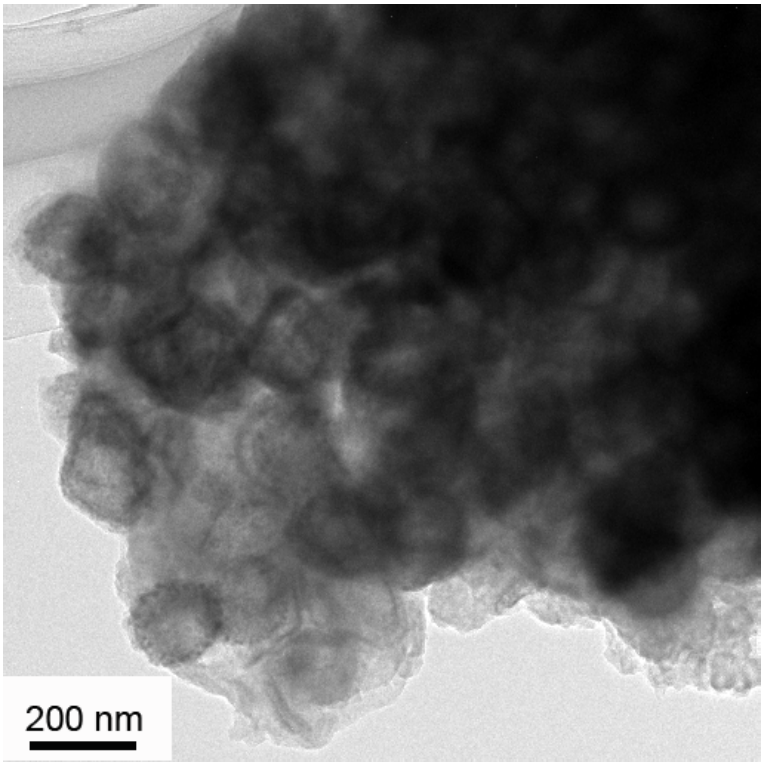

Figure S10. TEM image of the SnO_2-HNS/G electrode after rate capability testing.

References:

1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
2. W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62.
3. X. W. Lou, C. Yuan and L. A. Archer, *Small*, 2007, **3**, 261.