

Supporting Information

Graphene-templated formation of 3D tin-based foams for lithium ion storage application with long lifespan

Bin Luo, Tengfei Qiu, Long Hao, Bin Wang, Meihua Jin, Xianglong Li, and Linjie Zhi*

Key Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology, China, Beiyitiao No. 11, Zhongguancun, Beijing, 100190, P. R. China.

E-mail: zhilj@nanoctr.cn

Experimental details

Material Synthesis: Graphene oxide (GO) was synthesized from natural graphite by a modified Hummers method.¹ G/SnO₂ hydrogels were prepared by an *in-situ* hydrolysis process of tin salts in a GO-containing ethylene glycol (EG)-water solution.² In a typical experiment, the as-synthesized GO (100 mg) was first suspended in 200 mL of a mixture of EG and water (volume ratio: 9: 1) that was hosted in a round-bottom flask, and then ultrasonically treated for 1 h, forming a brown dispersion. Then 4.0 g SnCl₂ · 2H₂O and 10 ml aqueous solution containing 0.8 g NaOH were added to the above dispersion subsequently. After magnetic stirring for 20 min, the solution was heated to 120 °C and refluxed for 4 h with constant stirring under atmospheric pressure. After that, the precipitate was filtrated and washed with deionized water for several times to remove the remaining reactants, resulting in a black hydrogel. The G/SnO₂ hydrogel was then subjected to freeze drying machine to produce F-G/SnO₂. For reference, R-G/SnO₂ was produced from the same hydrogel using a vacuum oven drying process.

For carbon coating, the G/SnO₂ composites were immersed in 30 mL of 0.5 M aqueous glucose solution with a 50 mL teflon autoclave, which was then heated in an electric oven at 180 °C for 10 h. The dark gray product was washed with deionized water and then dried in a vacuum oven at 80 °C. The carbon-coated G/SnO₂ (G/SnO₂@C) composites were then obtained

after annealing at 450 °C for 2 h in argon atmosphere. For reference, R-G/SnO₂@C was prepared by the same method using R-G/SnO₂ as precursor.

To prepare the SnO₂ and SnS₂ foams, the F-G/SnO₂ composite was first calcinated in air at 400 °C for 10 h to completely remove the underneath graphene matrix. The obtained SnO₂ foam was then heated at 300 °C for 5 hours under a gas mixture of H₂S and Ar (volume ratio: 1: 9) with a flow rate of 200 sccm.

Material Characterization: X-ray diffraction (XRD) with Cu K α radiation (Rigaku D/max-2500B2+/PCX system) was used to determine the phase composition and the crystallinity. The morphology and microstructure of the samples were investigated by FE-SEM (Hitachi S4800), FE-TEM (FEI Tecnai G2 20 ST), and TGA (Perkin Elmer, Diamond TG) measurements. Nitrogen cryoadsorption (77 K) was measured by using a ASAP 2020 physisorption analyzer (USA) and the sample was outgassed under vacuum at 200 °C for 10 h before measurement. The specific surface area was obtained by Brunauer-Emmett-Teller (BET) analyses of the adsorption isotherm. The apparent density, the mass per unit volume of material including voids inherent in the material, were calculated according to the mass and the physical dimensions of each sample. In detail, we carefully polished the freezing-dried or oven-dried samples into small cubes and then calculated the volume by measuring the side length. Here, the averaged values of data are used.

Electrochemical measurements were carried out in coin-type half-cells (2032 size). The working electrode was made from the as-prepared composites as active material, super P carbon black, and polyvinylidene fluoride (PVDF) binder in a weight ratio of 80:10:10 on a copper foil. After drying, the electrode was roll-pressed to increase their density. The electrolyte was 1 M LiPF₆ with 1:1 ethylene carbonate: diethylene carbonate (EC: DEC), and the counter and reference electrodes were made from lithium foils. The cells were assembled in an argon-filled glovebox with the concentrations of moisture and oxygen below 0.1 ppm. Galvanostatic

charge/discharge measurements of the devices were performed on a multichannel battery testing system (Wuhan LAND). Electrochemical impedance spectra (EIS) were obtained by applying a sine wave with amplitude of 5.0 mV over the frequency range from 100 kHz to 0.01 Hz.

All the testing current setting and specific capacity calculations were based on the SnO₂/C composite in the working electrodes. The areal (C_a) and volumetric capacity (C_v) of the electrode is calculated as follows, respectively:

$$C_a (\text{mAh cm}^{-2}) = C_g (\text{mAh g}^{-1}) * \rho_a (\text{mg cm}^{-2}) \quad (1)$$

$$C_v (\text{mAh cm}^{-3}) = C_g (\text{mAh g}^{-1}) * \rho_v (\text{mg cm}^{-3}) \quad (2)$$

Where C_g is the gravimetric capacity of the electrode, ρ_a and ρ_v are the areal density and volumetric density of the electrode which are estimated based on the measured weight and geometry of the electrode before being assembled into the cell. In detail, ρ_a and ρ_v are calculated by the following equations:

$$\rho_a (\text{mg cm}^{-2}) = m_{\text{electrode}} (\text{mg}) / S_{\text{electrode}} (\text{cm}^2) \quad (3)$$

$$\rho_v (\text{mg cm}^{-3}) = m_{\text{electrode}} (\text{mg}) / (S_{\text{electrode}} (\text{cm}^2) * t_{\text{electrode}} (\text{cm})) \quad (4)$$

Where $m_{\text{electrode}}$ and $S_{\text{electrode}}$ are the measured weight of the active material and the surface area the electrode, respectively. $t_{\text{electrode}}$ is the thickness of electrode film, which is measured from the cross sectional SEM images of the electrodes as shown in Fig. S5.

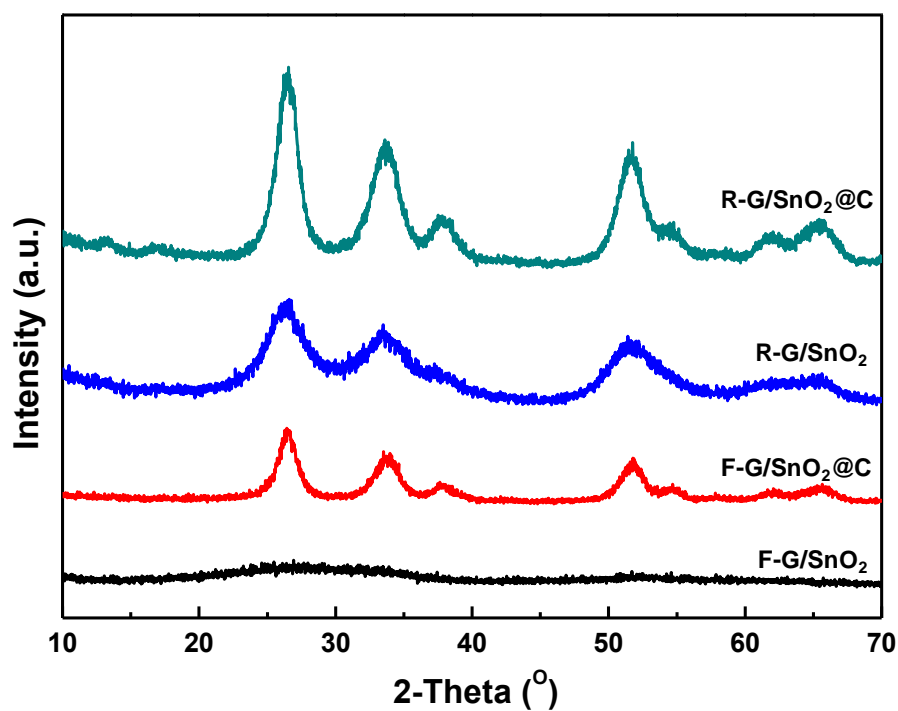


Fig. S1. XRD patterns of the F-G/SnO₂, F-G/SnO₂@C, R-G/SnO₂, and R-G/SnO₂@C composites, respectively.

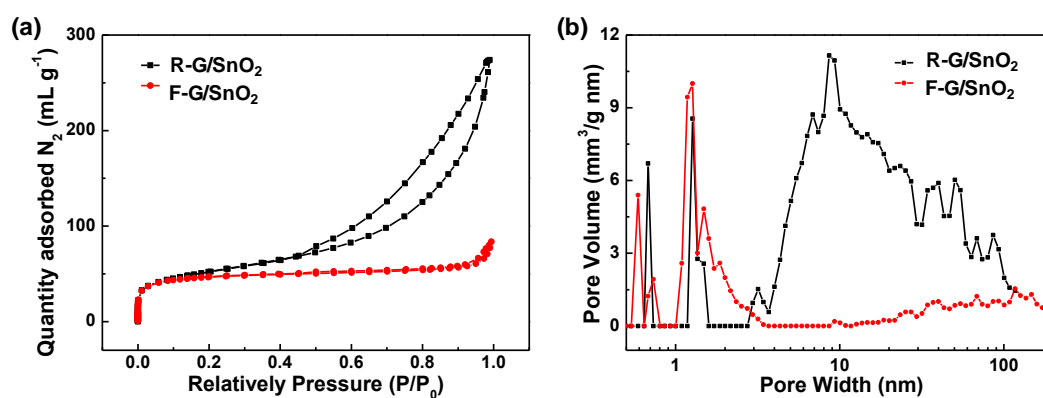


Fig. S2. Adsorption behaviors and surface nature of the R-G/SnO₂ and F-G/SnO₂ composites. e) Nitrogen adsorption isotherms and f) pore size distributions (PSD) of these two G/SnO₂ composites

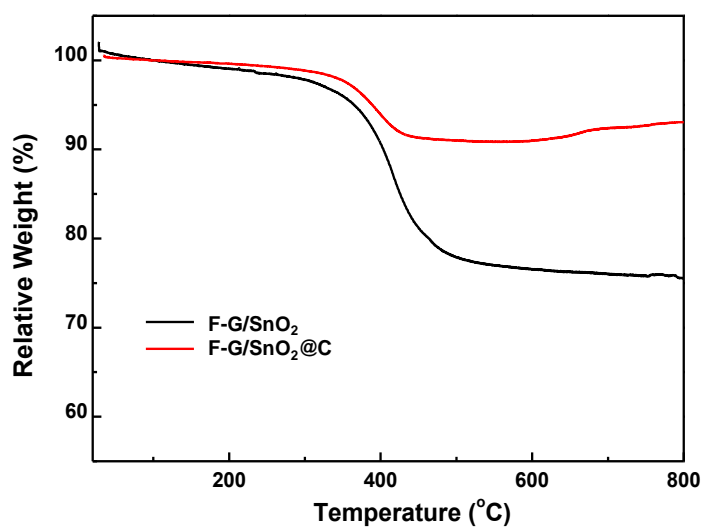


Fig. S3. Thermal gravimetric analysis (TGA) of the as-prepared F-G/SnO₂ and F-G/SnO₂@C composites. The SnO₂ contents of F-G/SnO₂ and F-G/SnO₂@C estimated from the thermal analysis are ca. 92.0 wt % and 75.8 wt %, respectively. The analysis was taken in air using a heating rate of 10°C min⁻¹.

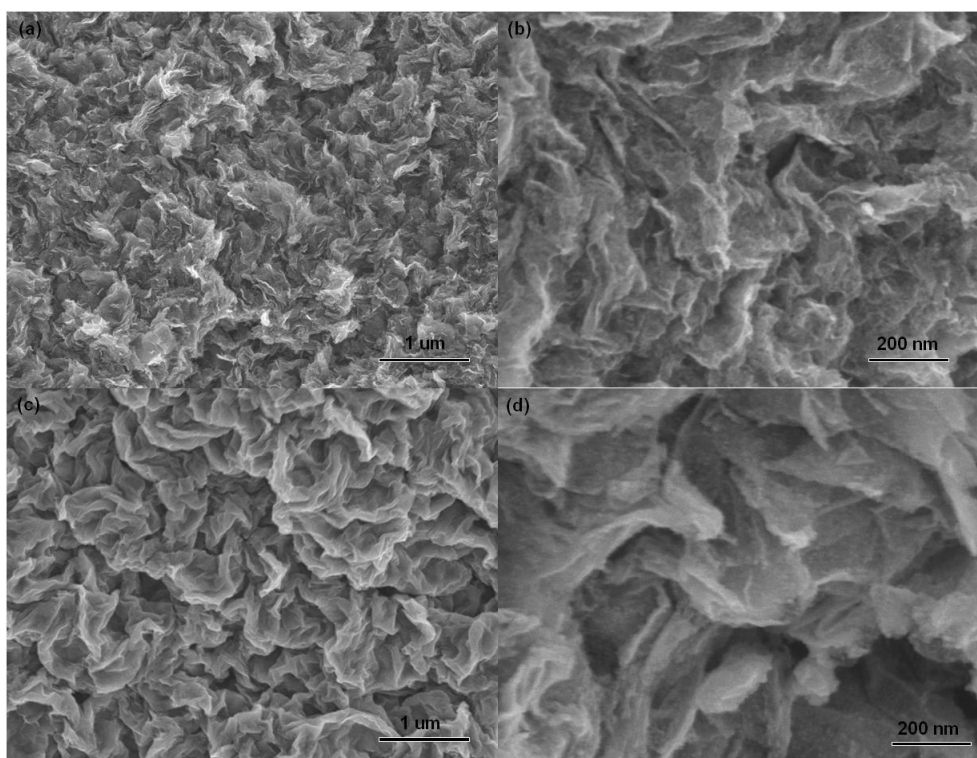


Fig. S4. SEM images of a, b) R-G/SnO₂ and c, d) R-G/SnO₂@C nanocomposites.

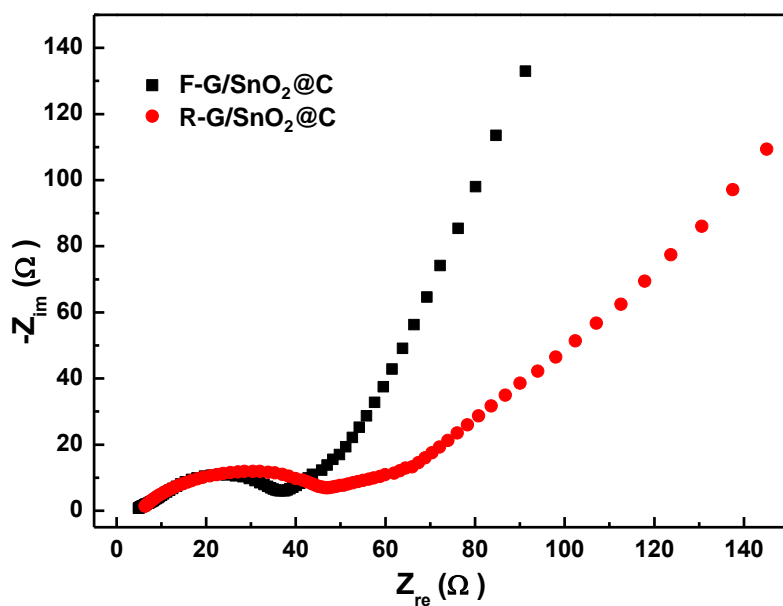


Fig. S5. Nyquist plots of F-G/SnO₂@C and R-G/SnO₂@C anodes in Li-ion batteries after 100 cycles obtained by applying a sine wave with amplitude of 5.0 mV over the frequency range from 100 kHz to 0.01 Hz.

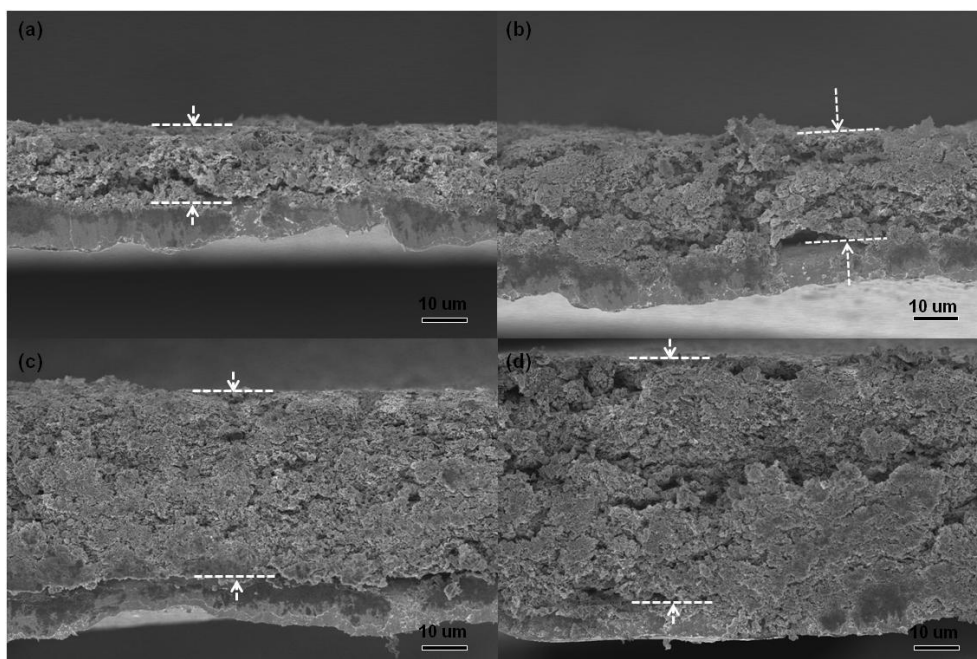


Fig. S6. SEM images of F-G/SnO₂@C electrodes with different thicknesses of a) 15 μm, b) 25 μm, c) 39 μm, and d) 52 μm.

Table S1. Detailed information of the above F-G/SnO₂@C electrodes

F-G/SnO ₂ @C Electrodes	a	b	c	d
ρ_a (mg cm ⁻²)	~0.9	~1.6	~2.5	~3.4
t (μ m)	~15	~25	~39	~52
ρ_v (g cm ⁻³)	0.60	0.64	0.64	0.65

Note: ρ_a is the areal mass loading of active material, t is the measured thickness of the electrode, and ρ_v ($\rho_v = \rho_a \cdot t$) is the calculated tap density of the active material in the electrode.

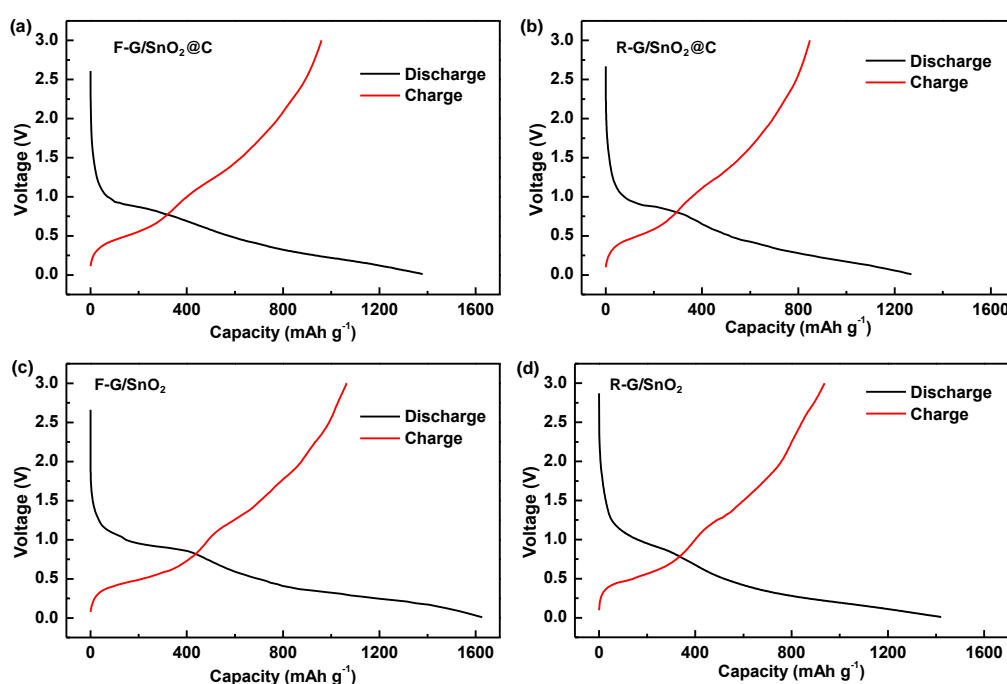


Fig. S7. Voltage profiles of the first charge/discharge process of a) F-G/SnO₂@C, b) R-G/SnO₂@C, c) F-G/SnO₂, and d) R-G/SnO₂, respectively. Two plateaus are present at approximately 0.9 and 0.3 V in the first discharge curve. The former might be ascribed to the formation of the solid electrolyte interface (SEI) and Li₂O resulting from the reduction of SnO₂ to Sn which are the main causes of the initial capacity loss.³ The other plateaus at 0.3 V is attributed to the alloying process between lithium and metallic tin.

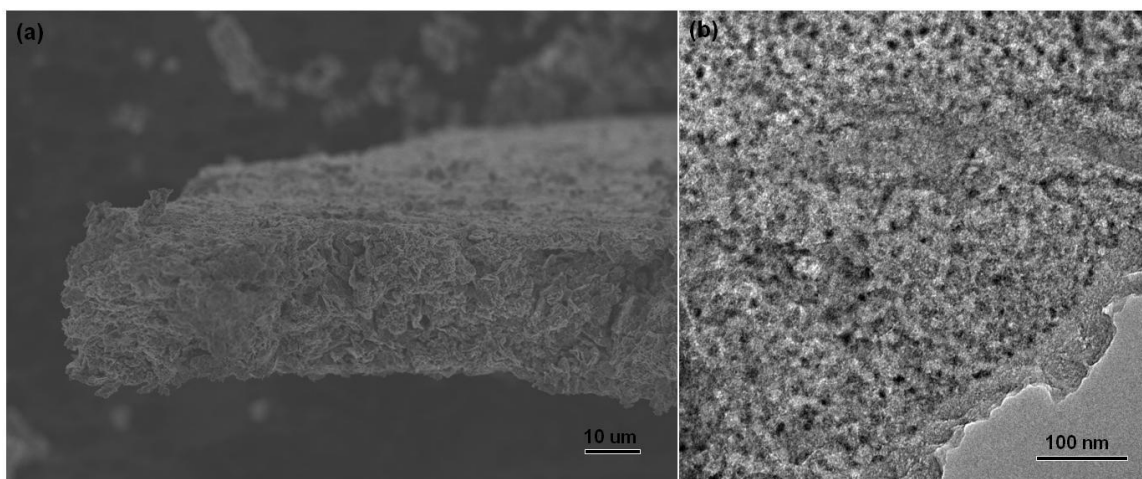


Fig. S8. a) Cross-sectional SEM image and b) TEM image of F-G/SnO₂@C electrode after 100 cycles.

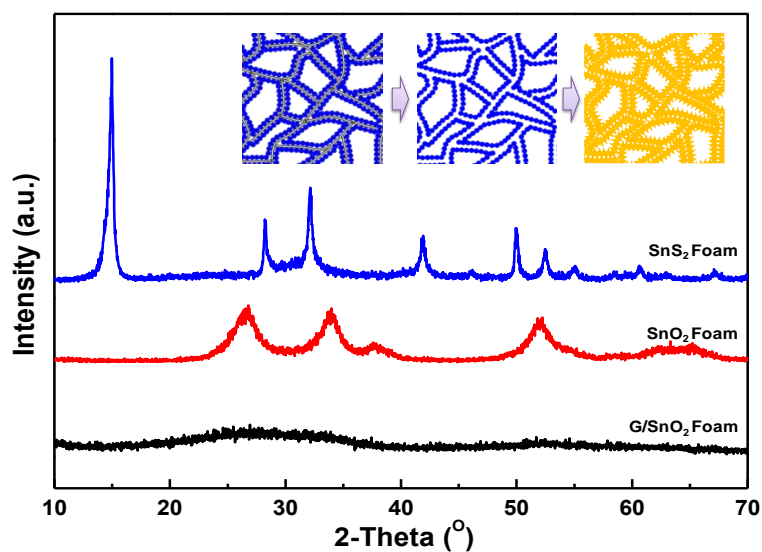


Fig. S9. XRD patterns of the F-G/SnO₂, F-SnO₂, and F-SnS₂.

- 1 W. S. Hummers and R. E. Offeman, *Journal of the American Chemical Society*, 1958, **80**, 1339-1339.
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- 3 X. W. Lou, Y. Wang, C. L. Yuan, J. Y. Lee and L. A. Archer, *Advanced Materials*, 2006, **18**, 2325.