Supporting Information

Nanospace-confined formation of flattened Sn sheets in pre-seeded graphenes for lithium ion batteries

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1. Sample preparation

In a typical procedure, graphite oxide (80 mg), which was prepared by using the modified Hummer’s method, was dispersed in deionized water (80 mL) to form a homogenous graphene oxide (GO) hydrosol by strong sonication (200 W, JY92-N, a high-energy bench mounted ultrasonic disintegrator) for 2 h. At the same time, SnCl₄·5H₂O (100 mg) was dissolved in a 10 mL PVA (1 mg mL⁻¹) solution under sonication for 5 minutes to form a SnCl₄/PVA homogeneous dispersion. Then, the SnCl₄/PVA dispersion was dropwised into the GO hydrosol under sonication and then stirred for 24 h at room temperature to form a uniform GO/SnCl₄/PVA mixture. Then, the mixture was vacuum-filtered using cellulose acetate membranes (pore diameter: 0.2 μm) to form a GO/Sn⁴⁺ hybrid membrane, which was washed with deionized water continuously. After the membrane was dried, it was thermally treated at 900 °C in an Ar atmosphere for 2 h at the heating and cooling rates of 5 °C/min to obtain the flexible G/Sn-L membrane. During this process, all the Sn⁴⁺ ions were transformed into Sn without loss since it was hard for the Sn to evaporate at 900 °C due to its low vapour pressure (~ 10⁻⁴ mmHg at 923 °C).¹ In order to decrease the size and thickness of the Sn nanosheets,
the G/Sn-L membrane was re-thermal treated at 300°C for 1 h in air and then immersed into the liquid nitrogen rapidly to obtain the G/Sn-S.

For control samples, the above-mentioned uniform GO/SnCl\textsubscript{4}/PVA mixture was frozen and suffered a freeze-drying to obtain a GO/Sn\textsuperscript{4+} hybrid. Then, such hybrid was thermal treated with the same procedure as that of G/Sn-L to obtain the G/Sn-F.

2. Characterization

Scanning electron microscopy (SEM) observations were conducted with a Hitachi S-4800 instrument (Hitachi, Japan). Transmission electron microscopy (TEM) observations were conducted with JEM-2100F instrument (JEOL, Japan). X-ray diffraction (XRD) measurements were collected at room temperature using the reflection mode (D8 FOCUS, Cu K\textalpha radiation, \(\lambda = 0.154 \text{ nm}\)). Raman spectra were recorded using a micro-Raman spectroscope (Jobin-Yvon LabRAM HR800, Horiba) with 633 nm incident radiation and a 50× aperture. Thermogravimetric analysis (TG, Rigaku, Japan) measurements were performed in air atmosphere to calculate the Sn fraction in the hybrids. AFM observation was conducted for dispersed samples dropped on freshly cleaved mica surfaces (ScanAsyst mode, Dimension Icon, Bruker, USA). The conductivity of the membrane was measured by a four-probe method.

3. Electrochemical measurements

Since the integrated membrane is hard to be infiltrated by the electrolyte, which induces large polarization during the charge/discharge process, it cannot present the true electrochemical performance of this hybrid structure when the membrane is used as the electrode directly. Therefore, for the electrochemical measurements, G/Sn-L and G/Sn-S hybrid membranes were ground into powders and then were mixed with acetylene black and poly (tetrafluoroethylene) (PTFE) in a weight ratio of 80:10:10 with the help of ethanol. After the grind process, the sandwich structure is also well maintained, which can be proved by the
SEM images shown in Fig. S10. And the mixture was pasted onto the nickel foam (1.77 cm²) with an active mass loading of about 1.0 mg cm⁻². The as-prepared nickel foam electrode was dried at 80 °C overnight and was pressed at a pressure of 5 MPa and then dried again at 80 °C overnight to act as working electrode. In order to verify the structure stability and make it easy to be compared after cycling, the membrane was also tailored and used as the electrode directly without binder or conductivity additives.

2032 coin-type half-cells were assembled using the prepared working electrodes in a high-purity argon-filled glove box. Lithium foils were used as the counter and reference electrode and a microporous polyethylene film was used as the separator. The electrolyte was 1 M lithium hexafluorophosphate (LiPF₆) dissolved in ethylene carbonate (EC)/dimethyl methyl carbonate (DMC) (1:1 by volume). Cyclic voltammogram (CV) measurement was performed on an electrochemical workstation (VMP3, Bio-Logic, France) with a voltage range from 0.005 V to 3.0 V at a scan rate of 0.1 mV/s. The electrochemical impedance spectroscopy (EIS) was carried out with the frequency range from 100 kHz to 10 mHz on the electrochemical workstation by applying a 5 mV of AC oscillation. Galvanostatic charge and discharge experiments and the cyclic tests of the coin cells were conducted using a battery tester (LAND 2001 CT) at different current densities with the potential window of 0.005 V to 3.0 V.

4. Supplementary Figures

![Fig. S1](image1.png)  ![Fig. S2](image2.png)

**Fig. S1** The surface (a) and cross-sectional (b) SEM images of G/Sn-L hybrid membrane.
Fig. S2 The SEM (a), XRD pattern (b) and TEM (c, d) images of G/Sn-F.

Fig. S3 Raman spectra of the G/Sn-S, G/Sn-L and G/Sn-F.
Fig. S4 The AFM images of G/Sn-S hybrid membrane with mild sonication. (a) The height AFM image; (b) the phase image corresponding to the image of (a); (c) the cross-section thickness contour profile.

Fig. S5 The XRD pattern of the pure graphene membrane.
Fig. S6 TG profiles of G/Sn-L and G/Sn-S hybrid membrane. Assuming that the TGA heating finally produces SnO$_2$, the Sn contents of G/Sn-L and G/Sn-S are determined to be about 51 and 46 wt%, respectively based on the following equation:

$$\text{Sn (wt\%)} = 100 \times \frac{\text{molar weight of Sn}}{\text{molecular weight of SnO}_2} \times \frac{\text{final weight of SnO}_2}{\text{molecular weight of SnO}_2} \times \frac{\text{initial weight of graphene/Sn hybrid}}{\text{initial weight of graphene/Sn hybrid}}$$

Fig. S7 The CV curves of G/Sn-L (a) and G/Sn-F (b) at a scanning rate of 0.1 mV s$^{-1}$. 
**Fig. S8** The cross-sectional SEM image of G/Sn-S membrane after 100 cycles. (full lithiation state)

**Fig. S9** The Nyquist plots of G/Sn-S, G/Sn-L and G/Sn-F.
Fig. S10 The SEM images of G/Sn-S after grinding.

References: