

Electronic Supplementary Information

In situ growth of heterostructured Sn/SnO nanospheres embedded in crumpled graphene as an anode material for lithium ion batteries

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1. Experimental Section

1.1 Sample Preparation

Preparation of Sn/SnO/GNSs composite. In a typical procedure, 0.72 g of tin tetrachloride (SnCl_4 , Acros) was dissolved in 10.0 mL of deionized water (DI) and then mixed with 1.0 g sodium oleate (TCI, 95%). The mixture was aged at 358 K for 6 h, leading to the formation of tin oleate. Then, 8.0 g of sodium carbonate (Aldrich, 98%) was added to the above mixture. After gentle grinding, the mixture containing tin oleate was uniformly coated on the surface of sodium carbonate particles. The ground mixture was heated to 973 K with a ramping rate of 3 K min^{-1} under a N_2 atmosphere for 6 h. After being cooled down naturally, the product was washed with deionized water to remove the sodium carbonate and then dried at 353 K for 12 h.

Preparation of GNSs. For comparison, graphene nanosheets (GNSs) were also prepared from natural graphite flakes by a modified Hummers method. Typically, 1.5 g of NaNO_3 was added to H_2SO_4 (69 ml) under the ice-bath with stirring. After dissolving the reactants, 3.0 g of graphite was added to the solution. 9.0 g of KMnO_4 was then dispersed slowly into the mixture below the temperature 293 K. After removing the ice-bath, the mixture was maintained around 300 K for 2 h. Then, the mixture was allowed to be diluted to 420 ml by deionized water. Shortly after that, 30 % H_2O_2 (11 ml) was added to the system. The remaining mixture was centrifuged and washed with deionized water. Finally, the graphene was obtained by drying at 318 K and subsequent thermal expansion at 273 K.

Preparation of Sn/SnO/GNSs mechanical mixture. For comparison, Sn/SnO/GNSs mechanical mixture (Sn/SnO/GNSs-M) was also prepared by a simple calcinations method. Typically, 0.6 g of commercial Sn particles (Shanghai Chaowei Company), 0.2 g of commercial SnO particles (Shanghai Chaowei Company) and 0.2 g of GNSs were mixed and grounded for 10 min. The mixture was subsequently heated in a tube furnace at 973 K for 6 h under a flowing N_2 .

2. Characterization Results

2.1 Characterization. Scanning electron microscope (SEM) images were recorded on a Hitachi S-4800 field-emission scanning electron microscope at an acceleration voltage of 5.0

kV. Transmission electron microscopy (TEM) images were obtained on a JEM-200CX transmission electron microscope. The powder X-ray diffraction was collected on a Rigaku D/Max 2550 X-ray diffractometer with a Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Raman spectroscopy was collected on the Bruker Optics Senterra R200-L (Bruker, Germany). The X-ray photoelectron spectroscopy (XPS) was performed on a KRATOS AXIS Ultra X-ray photoelectron spectrometer. Photoemission spectra were obtained with an Mg K α radiation (1253.6 eV) and the standard deviation for the binding energy (BE) values is 0.1 eV. The nitrogen adsorption/desorption measurements were performed on an ASAP 2020 Accelerated Surface Area and Porosimetry (Micromeritics Inc., USA). The carbon content of the Sn/SnO/GNSs composite was obtained on a Vario EL III CHNS/O elemental analyzer.

2.2 Electrochemical Tests. The Sn/SnO/NGNSs composite (80 wt%), Super-P carbon black (5 wt%), and sodium carboxymethyl cellulose (CMC, 15 wt%) were mixed in water solution to form a slurry. The slurry was spread onto a Cu foil by a doctor blade method, followed by drying in a vacuum at 70 °C for 10 h. CR2032 coin cells were assembled in a glove box filled with ultra-high purity argon using polypropylene membrane (UBE Industries Ltd.) as the separator, Li metal as the anode, and 1 M LiPF₆ in ethyl carbonate/dimethyl carbonate (EC/DEC) (1:1 v/v) as the electrolyte. The galvanostatic charge and discharge experiment was performed with a battery tester LAND-CT2001A in the potential range of 0.01~3.0 V at room temperature. Electrochemical impedance spectroscopy (EIS) measurements were performed on a CHI 660B electrochemical workstation. Cyclic voltammetry (CV) was conducted on the workstation at a scanning rate of 0.1 mV s⁻¹ in a potential range of 0.01 V to 3.0 V (*vs.* Li/Li⁺).

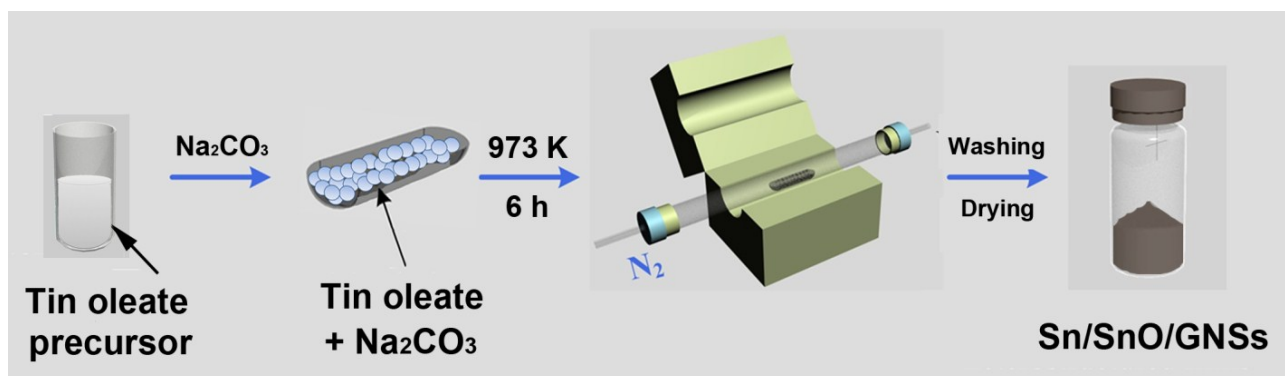


Figure S1. Synthesis procedure for the Sn/SnO/GNSs composite.

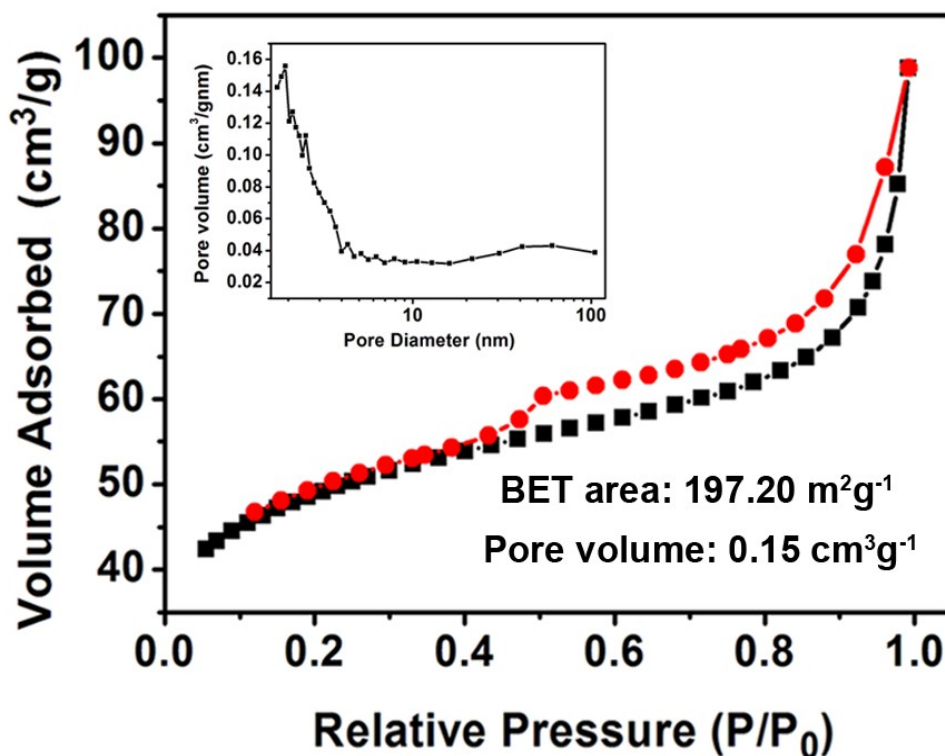


Figure S2. Nitrogen adsorption-desorption isotherm and the pore size distribution curve of the Sn/SnO/GNSs composite. The BET specific surface area is 197.20 m²g⁻¹, indicating their porosity structure with large surface areas. Generally, traditional GNSs prepared by a Hummers method have a pore volume as high as 2.8 cm³g⁻¹,^{S1} but to our Sn/SnO/GNSs composite, pore volume is only 0.15 cm³g⁻¹, indicating fully that most of void spaces in the crumple GNSs are embedded by Sn species.

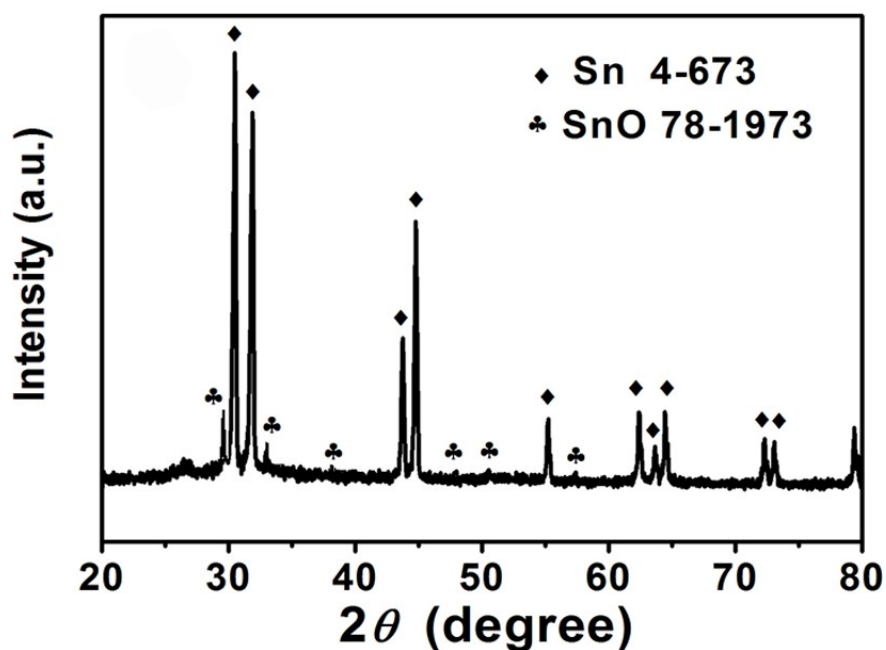


Figure S3. XRD pattern of the Sn/SnO/GNSs composite. Semi-quantitative XRD analysis shows the mass ratio of SnO and Sn in the composite is approximately 14: 86. Meanwhile, the carbon content of the Sn/SnO/GNSs composite was measured by elemental analyzer. Elemental analysis suggests that the carbon weights approximately 29 wt%. Combined with elemental analysis of C and semi-quantitative XRD analysis of Sn, the contents of Sn, SnO and graphene in the composites are approximately 61, 10 and 29 wt%, respectively.

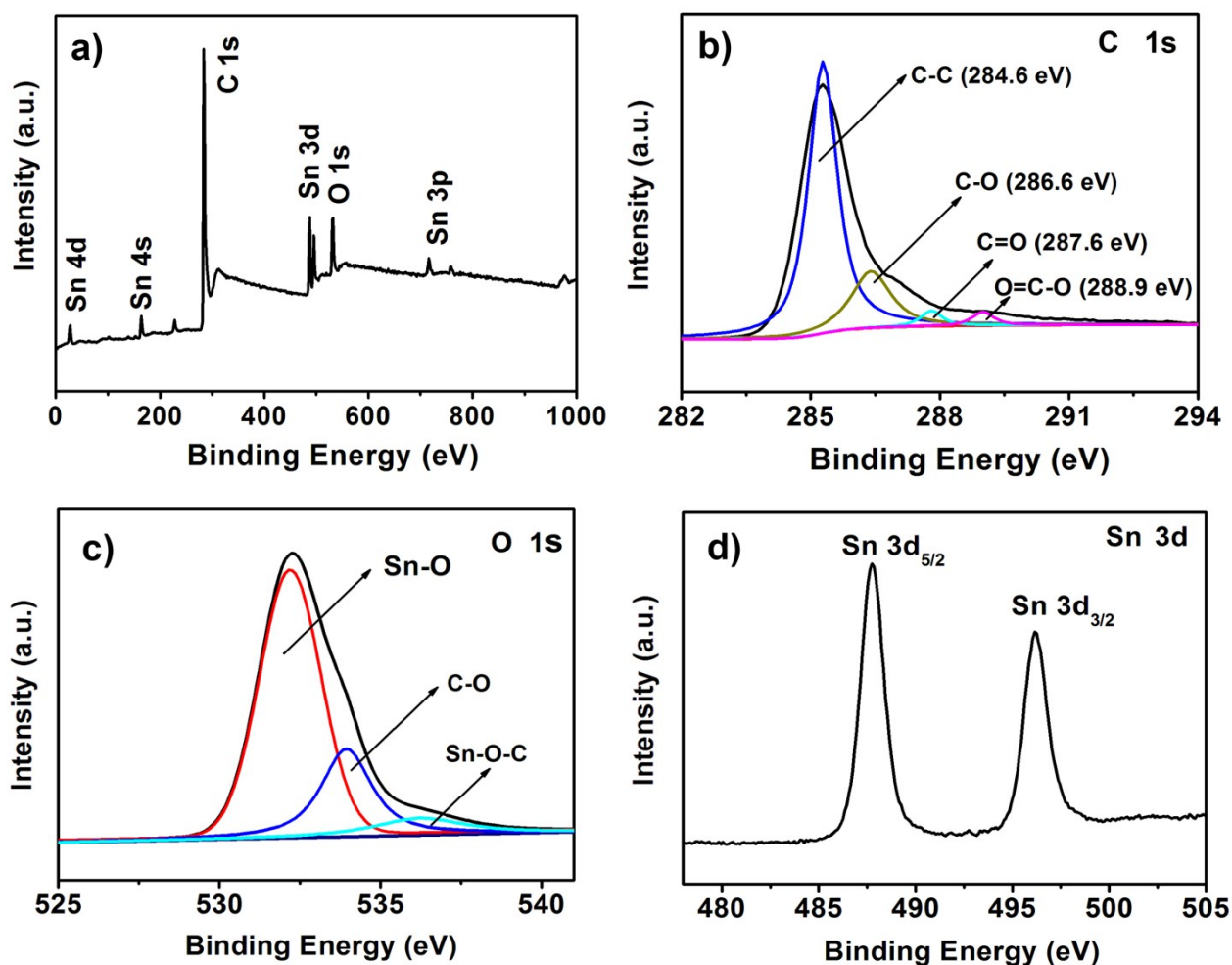
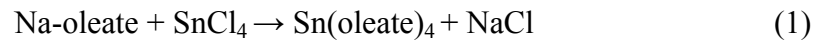


Figure S4. (a) The XPS survey spectrum, (b) C 1s, (c) O 1s and (d) Sn 3d deconvoluted spectra of the Sn/SnO/GNSs composite. The XPS full spectrum indicates that the Sn/SnO/GNSs composites are composed of C, Sn and O elements. It is speculated that the Sn and C species would origin from the precursor of Sn-oleate, and O would be introduced by tin oxides, in which the oxidation occurs on the surface of metallic Sn. The peak of O 1s spectrum at the binding energy of 532.1 eV was attributed to the Sn-O bonds present in the composites, and the small peak at 533.2 eV originated from the hydroxyl and epoxy groups present in graphene. Another small peak around 535.6 eV was assigned to the Sn-O-C bonds between the Sn spheres surface and graphene. Two symmetrical peaks of Sn 3d spectra appeared at 487.2 eV and 495.6 eV are attributable to Sn 3d_{5/2} and Sn 3d_{3/2}, respectively, characteristic for tin oxides.^{S2} Therefore, it is proposed the local CVD reaction was expected to take place to generate the Sn/SnO nanospheres and crumple GNSs simultaneously under the high temperature.



Supplementary Equation S1-6. The proposed reactions for the synthesis of Sn/SnO/GNSs.

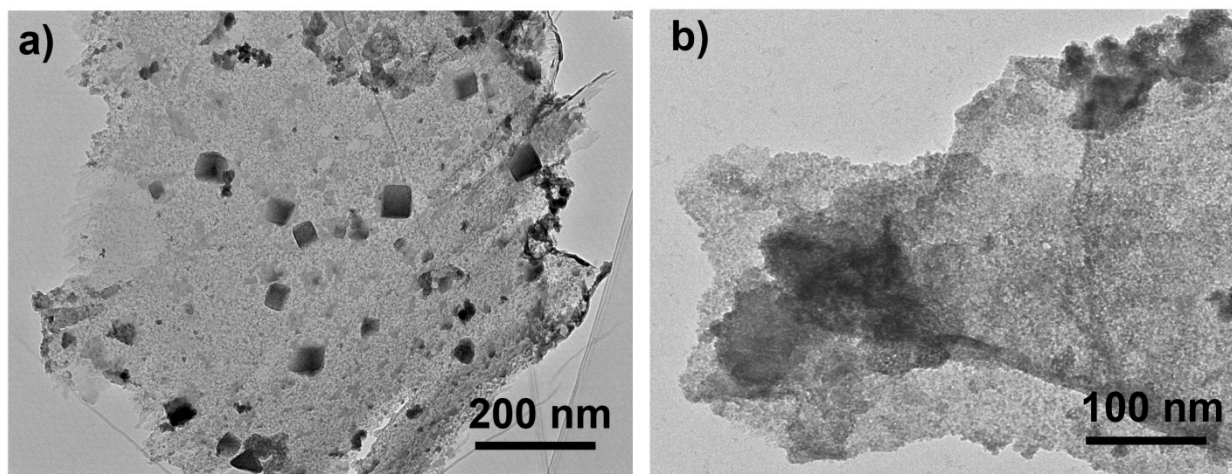


Figure S5. TEM images of (a) the products under the reaction temperature of 773 K for 6 hr and (b) the carbon layer obtained through removal of Sn species with acid-washing treatment.

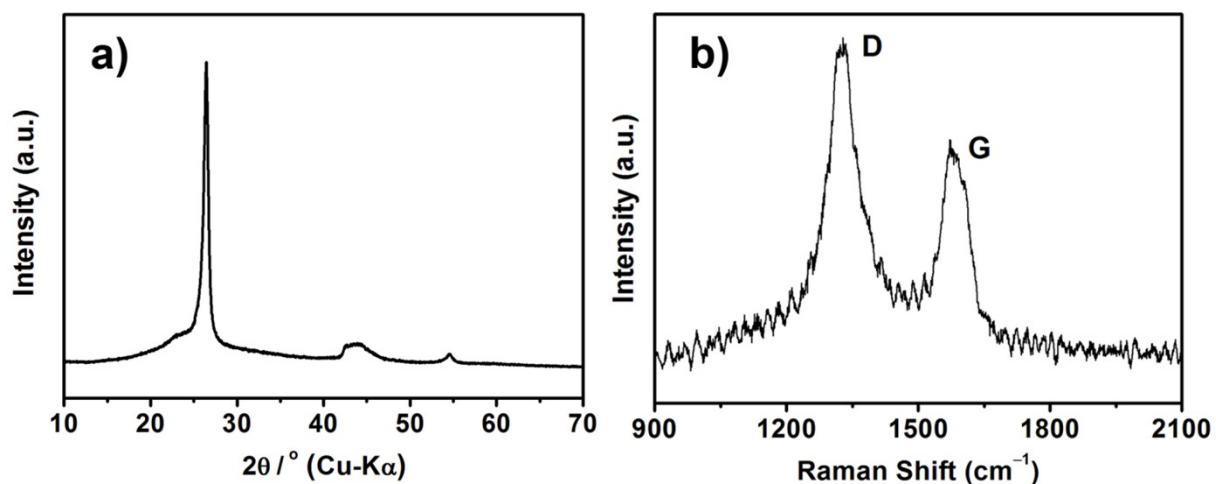


Figure S6. (a) XRD pattern and (b) their corresponding Raman spectrum of graphitized carbon obtained under the reaction temperature of 773 K. The result indicates that graphitized carbons are generated in the reaction system if the reactant temperature is relatively low.

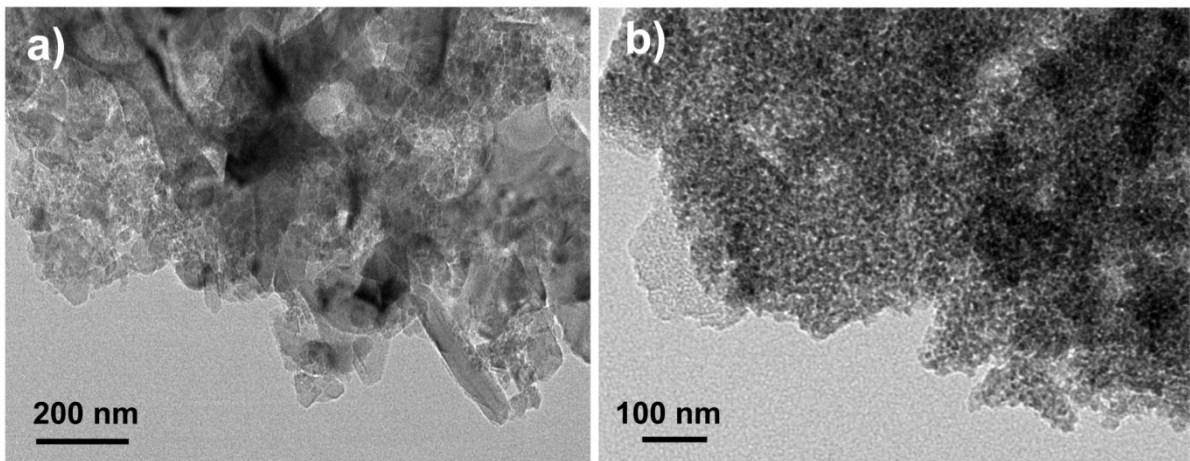


Figure S7. TEM images of (a) the products reaction time is less 1 h under 973 K and (b) their corresponding carbon layer obtained through removal of Sn species with acid-washing treatment.

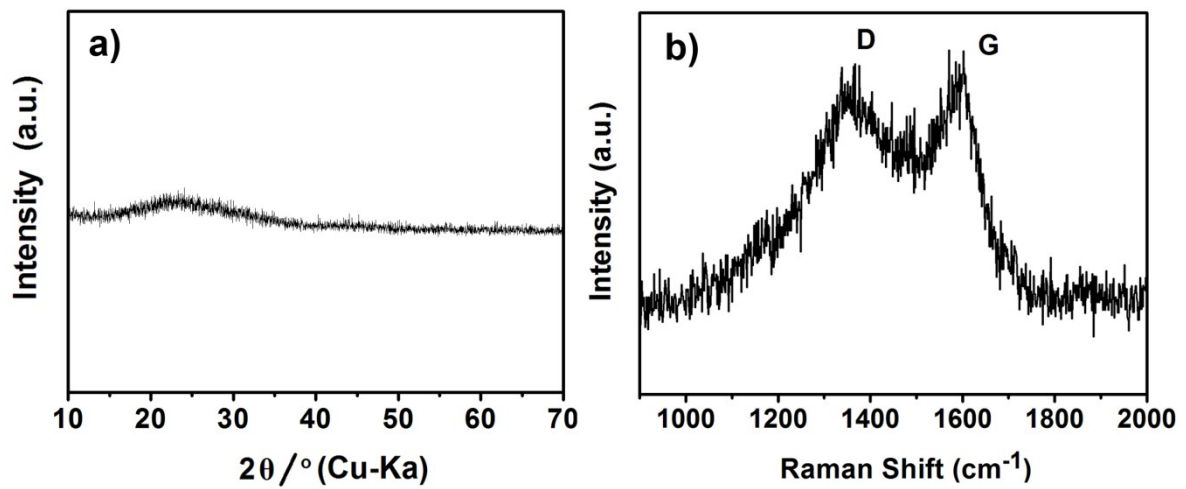


Figure S8. (a) XRD pattern and (b) their corresponding Raman spectrum of amorphous carbon obtained within reaction time of less 1 h. The result indicates that amorphous carbons are generated in the reaction system if the reactant time is less 1 h.

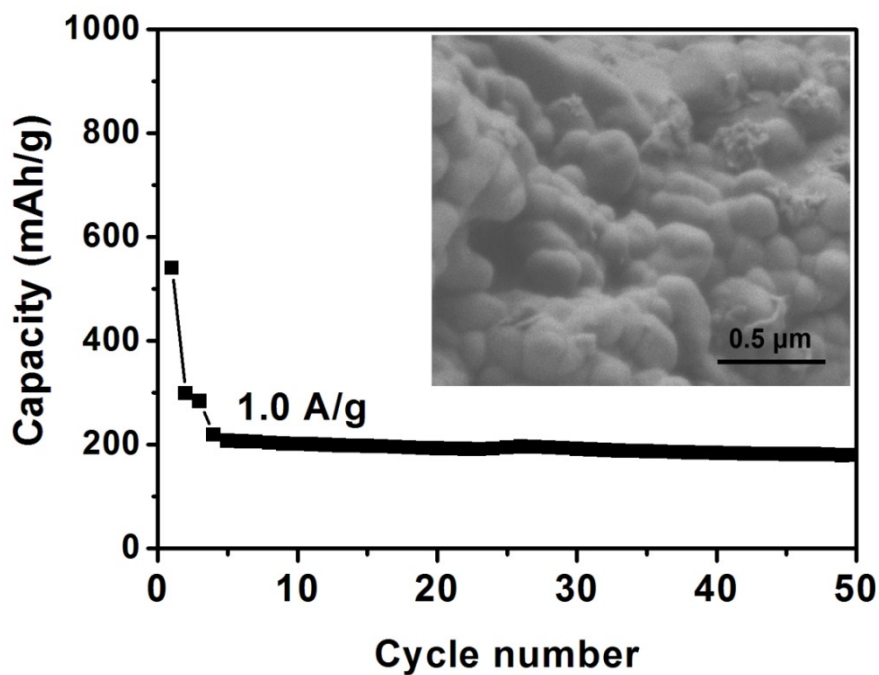


Figure S9. Cycling performance of our GNSs sample at a current density of 1.0 Ag^{-1} . The result exhibits the storage performance of Li^+ in crumple GNSs. Inset is the SEM image of the Sn/SnO/GNSs electrode after 50 cycles. This image shows a film covers the surface of the electrode material after 50 cycles, confirming the generation of solid electrolyte interface (SEI) layer.^{S3}

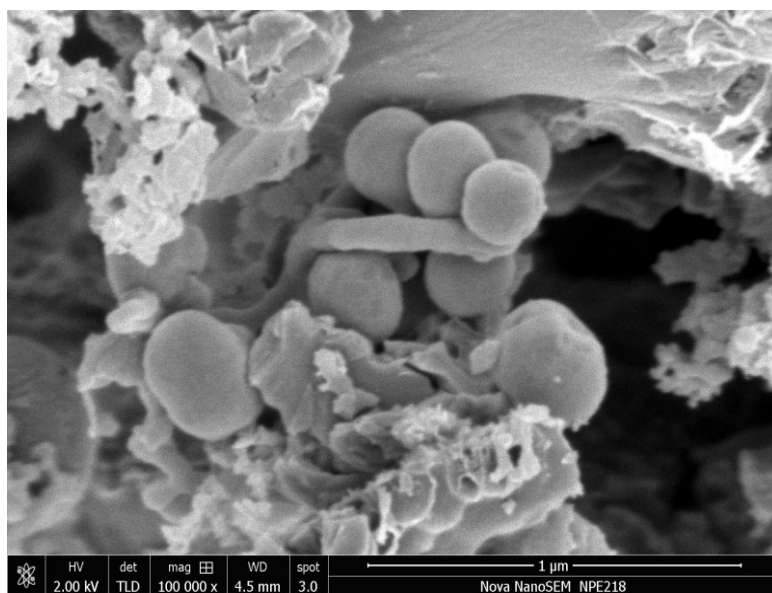


Figure S10. SEM image of the mechanical mixture of GNSs, commercial Sn and SnO nanoparticles.

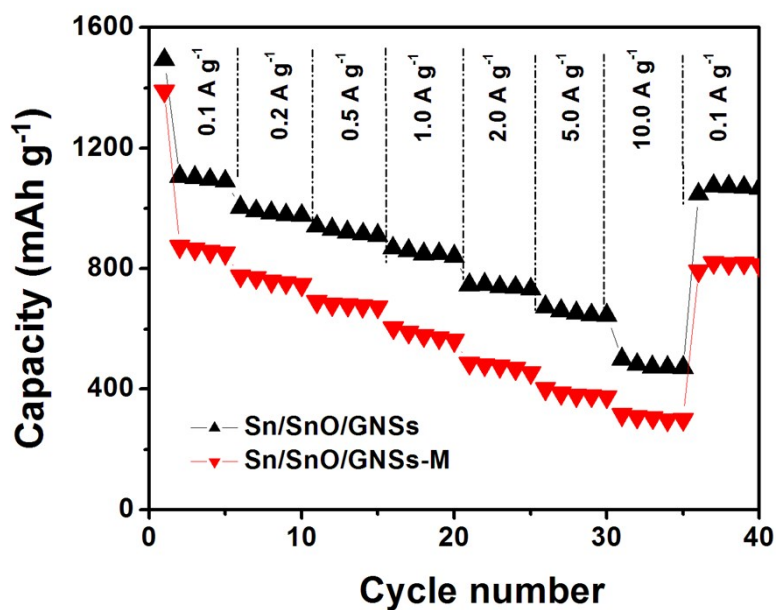


Figure S11. Rate performances at various current densities for the samples of Sn/SnO/GNSs and Sn/SnO/GNSs-M. The rate capability of Sn/SnO/GNSs-M is obviously inferior to that of our Sn/SnO/GNSs composite.

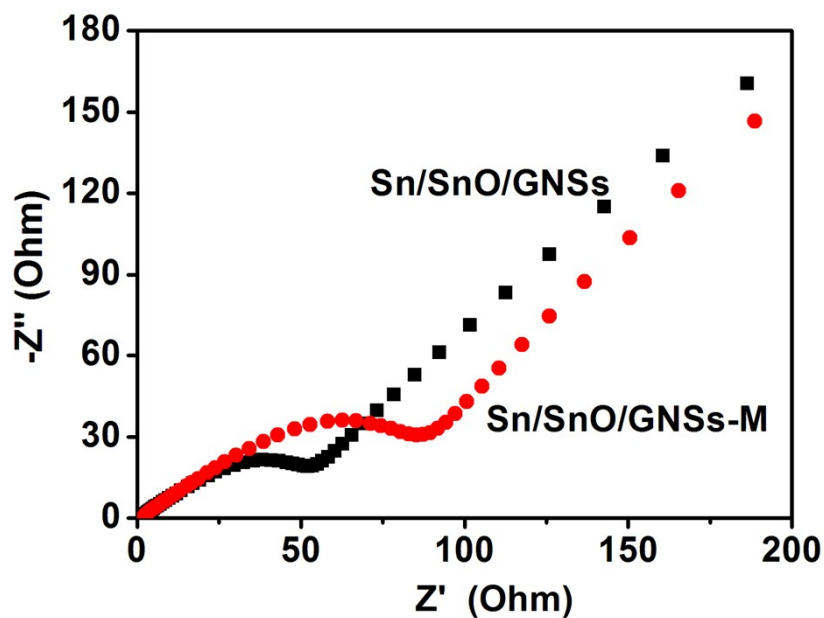


Figure S12. Electrochemical impedance spectra of the electrodes of Sn/SnO/GNSs and Sn/SnO/GNSs-M after cycling tests. It is shown that the resistance of the Sn/SnO/GNSs electrode is much smaller than that of the Sn/SnO/GNSs-M electrode.

References

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- [S2]. H. J. Ahn, H. C. Choi, K. W. Park, S. B. Kim and Y. E. Sung, Investigation of the structural and electrochemical properties of size-controlled SnO₂ nanoparticles, *J. Phys. Chem. B*, 2004, **108**, 9815-9820.
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