

Electronic Supplementary Information (ESI) for

Designed Synthesis of SnO₂-Polyaniline-Reduced Graphene Oxide Nanocomposites as an Anode Material for Lithium-Ion Batteries†

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Experimental Section

Synthesis of graphene oxide (GO): GO was synthesized using a modified Hummer's method from graphite powders (chemically pure, CP) with NaNO₃, H₂SO₄, and KMnO₄, as described elsewhere.^[S1] In a typical case, 3 g graphite powder was added into 69 ml of concentrated H₂SO₄, followed by adding 1.5 g NaNO₃ into above mixture under stirring and cooling in an ice bath condition. The mixture was continuously stirred while 9 g KMnO₄ was added slowly so as to keep the temperature of mixture below 20 °C. Then the mixture was kept at 35 °C for 30 min, followed by adding 137 ml deionized water while stirring without intermitting, and the temperature would rise up to 98 °C. The mixture was kept stirring for a further 15 min, and 420 ml deionized water and 30% H₂O₂ were added in sequence. The oxidized material was then washed with 1:10 (v:v) HCl solution one time and deionized water three times to remove metal ions, followed by centrifugation. The collected product was dried in a vacuum drying oven at 45 °C. The GO was obtained thereafter.

Synthesis of Polyaniline (PANI)@Graphene oxide (GO): 20 mg GO was added into 10 ml deionized water, followed by ultrasonic treatment for 3h. Then, 99.8% aniline (50 μl) and 1M HCl (20 ml) were added into above solution with stirring for 30 min. Ammonium persulfate (APS, 245.03 mg) was dissolved in 50 ml deionized water with stirring for 10 min. Then, ammonium persulfate solution was added into the GO-aniline mixed solution with stirring overnight under ice bath condition. The solid product was got after pumping sucking process, followed by washing with deionized water for three times.

Synthesis of SnO₂@Polyaniline (PANI)@reduced graphene oxide (RGO) (termed as SPG): All of the obtained PANI@GO solid powder was dispersed into 40 ml deionized water. Then, SnCl₄·5H₂O (884.01 mg) was dissolved into above dispersed liquid with stirring for 10 min to form solution A. Hexamethylenetetramine (or Urotropine, C₆H₁₂N₄, 353.56 mg) was dissolved into 40 ml deionized water with stirring for 10 min to form solution B. Solution B was added into solution A dropwise with stirring

for 2h, then, the mixture was sealed in a Teflon-lined stainless steel autoclave, and heated to 180 °C for 24 h. The product was separated from the mixture by pumping sucking process, followed by washing with deionized water for three times. After drying at 40°C, the SPG was obtained.

Synthesis of reduced graphene oxide (RGO): GO (80 mg) was added into 80 ml deionized water with ultrasonic treatment for 3h, followed by stirring for another 2h. Then, it was sealed in a Teflon-lined stainless steel autoclave, and heated to 180 °C for 24 h. The product was separated from the mixture by pumping sucking process, followed by washing with deionized water for three times. After drying at 40°C, the SPG was obtained.

Characterization: The phase structure was studied by X-ray diffractometer (Druker D8 Advance) with Cu K α radiation ($\lambda = 154056 \text{ \AA}$, operating at 40 kV \times 40 mA). Raman spectra (Renishaw, RM 1000) were measured with excitation from the 514 nm line of an Ar ion laser with a power of about 5 mW. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 560 FT-IR spectrophotometer. X-ray photoelectron spectra (XPS) were recorded on a PHI quantoera SXM with an Al K $\alpha = 280.00 \text{ eV}$ excitation source, where the binding energies were calibrated by referencing the C1s peak to reduce the sample charge effect. Transmission electron microscopy (TEM) was carried out on a Hitachi H-7650B, operating at 80 kV. High resolution electron microscopy (HRTEM) measurement was carried out on a JEOL JEM-2010 electron microscope, operating at 200 kV. Atomic force microscopy (AFM) analysis was carried out using a Digital Instruments Dimension 3100 microscope in the tapping mode with CMG samples coated on a Si surface.

Electrochemical experiments: Electrochemical experiments were performed using CR 2032 type coin cells assembled in an argon-filled glove box (MBRAUN). The working electrode was prepared by mixing the SPG and Carboxymethyl Cellulose Sodium (CMC, 3%) at a weight ratio of 90 : 10, followed by pasting on pure Cu foil (15 μm). Celgard 2400 was used as a separator. Lithium foil was used as the counter electrode. The electrolyte consisted of a solution of LiPF₆ (1 M) containing vinylene carbonate (2%) in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1 : 1 : 1, volume ratio). A galvanostatic cycling test of the assembled cells was carried out on a BS-9300K system in the voltage range of 0.001–3.0 V (vs. Li⁺/Li) at current density of 0.2 C (200 mA g⁻¹), 0.5, 1.0, 2.0, and 5.0 C, respectively. The weight of SPG in the working electrode was used to estimate the specific discharge capacity of the LIB, which was expressed in mA·h/g of SPG.

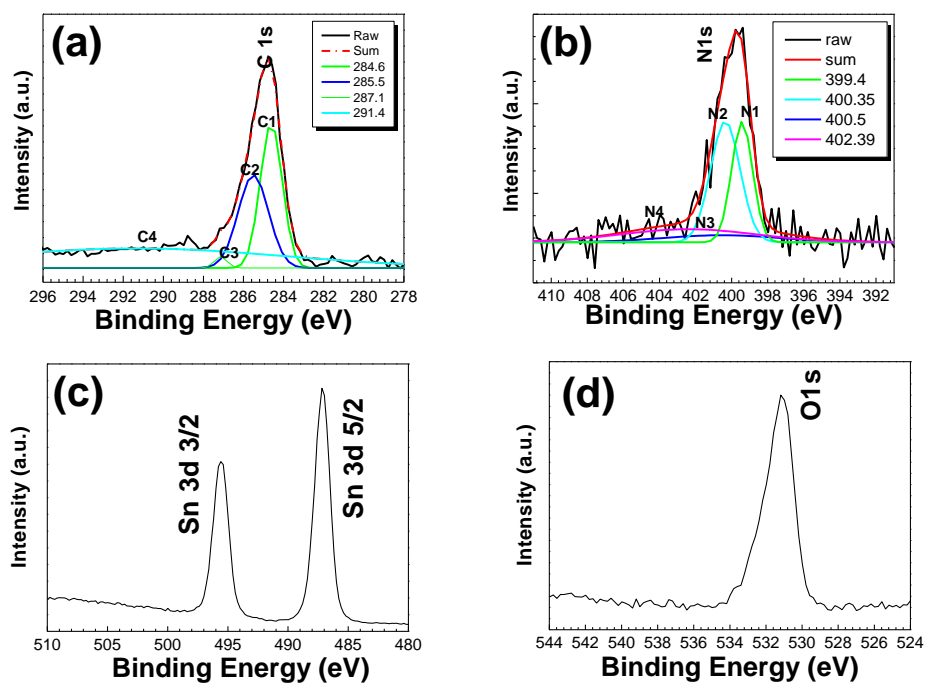


Fig. S1. XPS spectra of (a) C1s, (b) N1s, (c) Sn3d, (d) O1s.

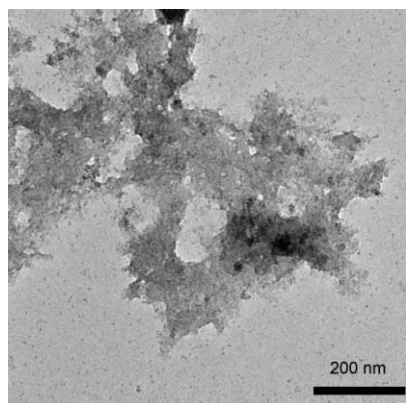


Fig. S2. TEM image of the structure of the SPG after the 50th cycle.

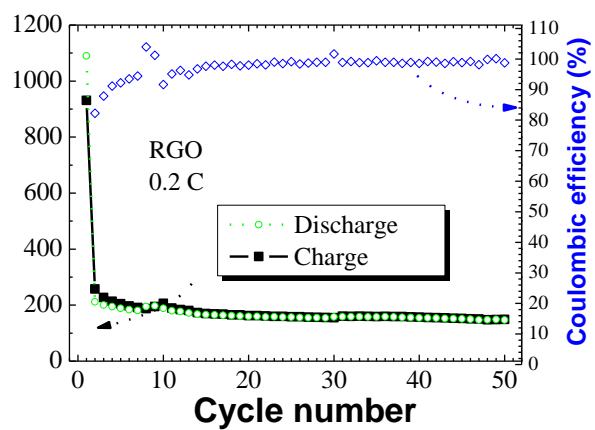


Fig. S3. Cyclic performances for RGO at 0.2C: charge and discharge capacitances as well as Coulombic efficiency as a function of cycle number.