Supporting information (SI)

Hierarchical Nanostructured Core-Shelled Sn@C Nanoparticles Embedded in Graphene Nanosheetes: Spectroscopic View and Its Application for Lithium Ion batteries

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Experimental

Sn@C-GNs synthesis

GNs were prepared applying a modified Hummers method to get graphene oxide first, and then performing the rapid heating of graphene oxide at 1050 °C at Ar atmosphere.[1,2] In a typical process of synthesizing Sn@C-GNs composites, the as prepared 80 mg GNs and 400 mg SnO_2 (325mesh, Aldrich) were ultrasonically dispersed into 40 mL ethanol solution for 30 min first. Then the suspension were filtered and dried at 80 °C overnight to collect SnO_2/GNs composites. The as-obtained SnO_2/GNs were put in a tube furnace and heat treated at 800 °C for 30min at 200 sccm gas mixtures (10% ethylene and 90% argon) atmosphere to realize the in-situ formation of Sn@C-GNs composites. After cooling to room temperature with pure Ar, Sn@C-GNs nanostructure was obtained. For Sn@C composites, the procedures are the same except the addition of GNs.

Characterization

The as-obtained products are characterized by powder X-ray diffraction (XRD, Rigaku RU-200BVH with a Co-Kα source (λ=1.7892 Å)), field emission scanning electron spectrometry (FE-SEM, Hitachi 4800S) coupled with energy dispersive spectroscopy (EDS), transmission electron microscope (TEM, Hitachi H-7000), and high resolution TEM (HRTEM, JEOL 2010 FEG microscope) and raman microspectroscopy (HORIBA Scientific LabRAM HR Raman spectrometer) with incident laser beam at wavelength of 532.03 nm under ambient condition. The carbon contents (wt %) were calculated by thermogravimetric analysis (TGA; Netzsch) in air from room temperature to 700 ^{o}C. The XANES experiments on the Sn L_3 and C Kedge were conducted on the undulator Soft X-ray Microcharacterization Beamline (SXRMB) and Spherical Grating Monochromator (SGM) beamline at the Canadian Light Source (CLS) located at the University of Saskatchewan in Saskatoon, which were recorded in total electron yield (TEY) using specimen current and X-ray fluorescence yield (FLY) using a Multi-Channel Plate.[3] Sn M edge spectra and extended X-ray absorption fine structure (EXAFS) data were obtained from the X-ray Science Division (XSD) partnered with the Pacific Northwest Consortium (PNC) at

Sector 20 of Advanced Photon Source, which were recorded in transmission mode.

Electrochemical Measurement

The as-prepared samples were mixed with conductive carbon black and polyvinylidene fluoride in a weight ratio of 8:1:1 in N-methylpyrrolidinone (NMP) solvent. After working electrodes were dried at 80 °C under vacuum overnight, the coin cells were assembled using lithium metal foil as the counter electrode and the polypropylene as the separator inside an argon-filled glove box. The electrolyte was 1M $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) solvent (1:1 volume ratio). The profiles of galvanostatically charging and discharging curves were obtained on a computer controlled battery tester system (Arbin BT-2000) at a voltage range of 0.01 to 3 V (vs. Li^+/Li) with a current density of 75 mA g^{-1}. Cyclic voltammetry (CV) measurements were performed on an electrochemical workstation (Potentiostat/Galvanostat/EIS (VMP3)) at a scanning rate of 0.1 mV s^{-1}.

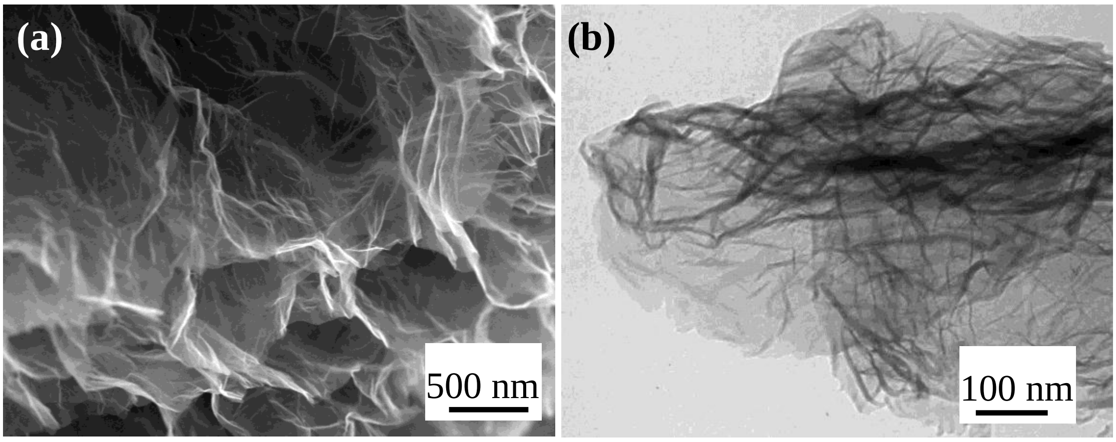

Figure S1. SEM image (a) and TEM image (b) of GNs.

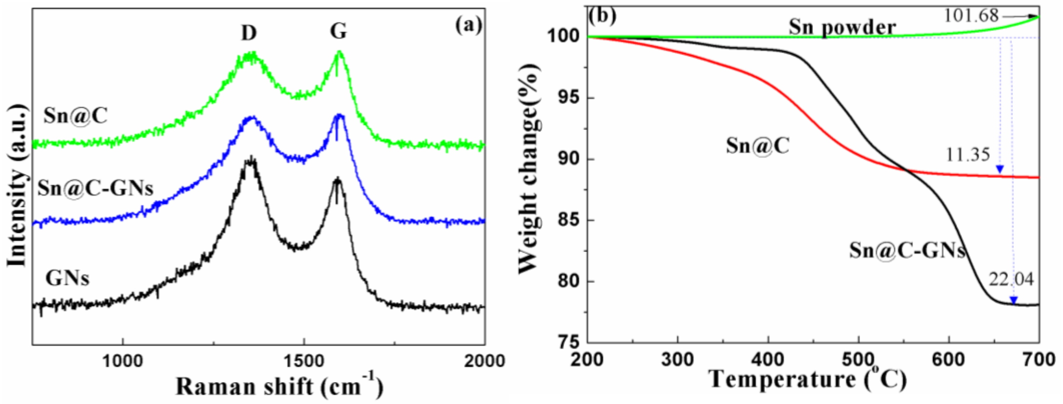

Figure S2. (a) Raman spectra of Sn powder, Sn@C and Sn@C-GNs; (b) TGA curves of Sn@C, Sn@C-GNs and GNs.

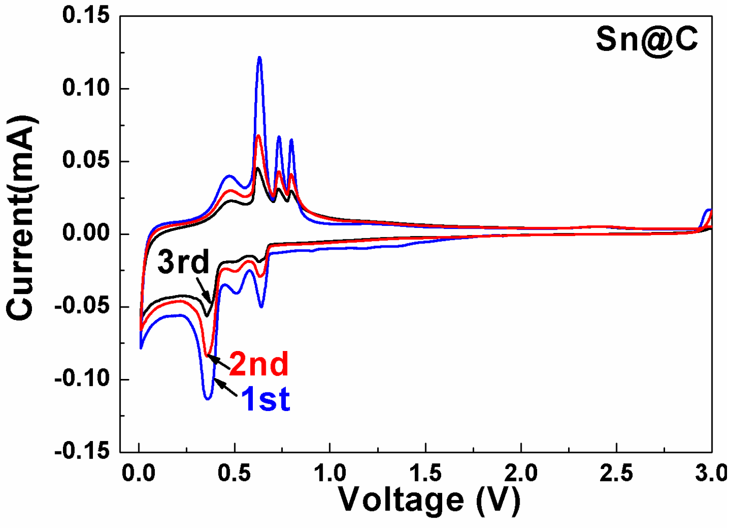

Figure S3. Cyclic voltammogram (CV) of Sn@C composites.

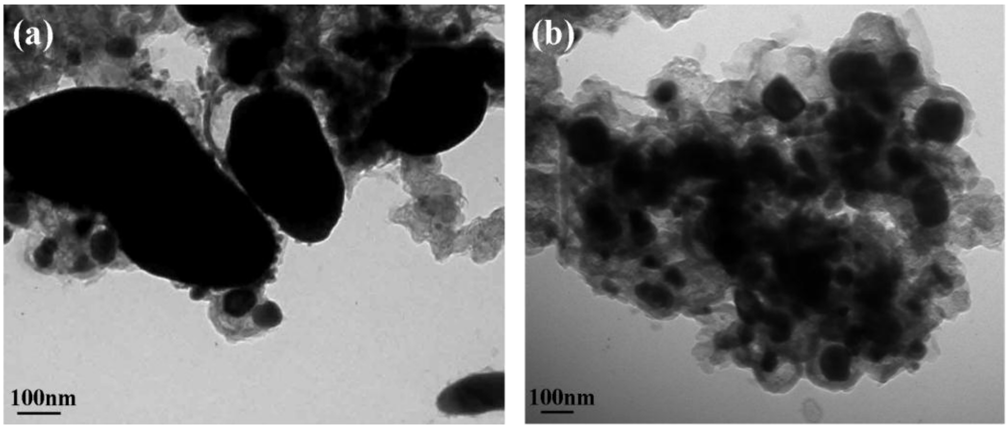

Figure S4. TEM image of Sn@C (a) and Sn@C-GNs (b) after 100 cycles.

1 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

2 D. Geng, Y. Chen, Y. Chen, Y. Li, R. Li, X. Sun, S. Ye, S. Knights. *Energy Environ. Sci.*, 2011, **4**, 760-764.

3 T. Regier, J. Paulsen, G. Wright, I. Coulthard, K. Tan, T. K. Sham and R. I. R. Blyth, *AIP Conf. Proc.*, 2007, **879**, 473.