Supporting information (SI)

Layer by Layer Assembly of Sandwiched Graphene/SnO_2 Nanorod/Carbon Nanostructures with Ultrahigh Lithium Ion Storage Properties

Dongniu Wang,[1.2] Jinli Yang,[1] Xifei Li,[1] Dongsheng Geng,[1] Ruying Li,[1] Mei Cai,[3] Tsun-Kong Sham*[2] and Xueliang Sun*[1]

[1]*Department of Mechanical and Materials Engineering, University of Western Ontario, London, Ontario, N6A 5B9 Canada. Email: xsun@eng.uwo.ca; Tel: +1 519 661-2111 ext. 87759*

[2]*Department of Chemistry, University of Western Ontario, London, Ontario, N6A 5B7 Canada. Email: tsham@uwo.ca; Tel: +1 519 661-2111 ext. 86341*

[3]*General Motors R&D Center, Warren, 48090-9055, MI, USA*

Experimental

Synthesis of Graphene, SnO_2 nanoparticle/Graphene (G/SnO_2 NP), SnO_2 nanorod/Graphene (G/SnO_2 NR)

The detailed procedures for prepare graphene from graphene oxide and G/SnO_2 NP can be found in previous published paper[1]. In a typical process of construction for G/SnO_2 NR hybrids, the as prepared 16 mg G/SnO_2 NP were ultrasonically dispersed into 20 mL stannate aqueous solution (0.5 mmol $SnCl_4$ and 8 mmol NaOH, Sigma-Aldrich.) vigorously for 30 minutes. Then the suspension was transferred into 50 mL high pressure Teflon-lined autoclave. The solution was subsequently heated to

200 °C and kept for 2h to facilitate the growth of SnO_2 nanorod. After rinsed with large amount of distilled water and ethanol to remove the sodium and choloride ions, the as-obtained G/SnO_2 NR hybrids were collected after final drying at 100 °C overnight for use in next step.

Synthesis of carbon coated SnO_2 nanorodGraphene (G/SnO_2 NR/C) nanocomposites

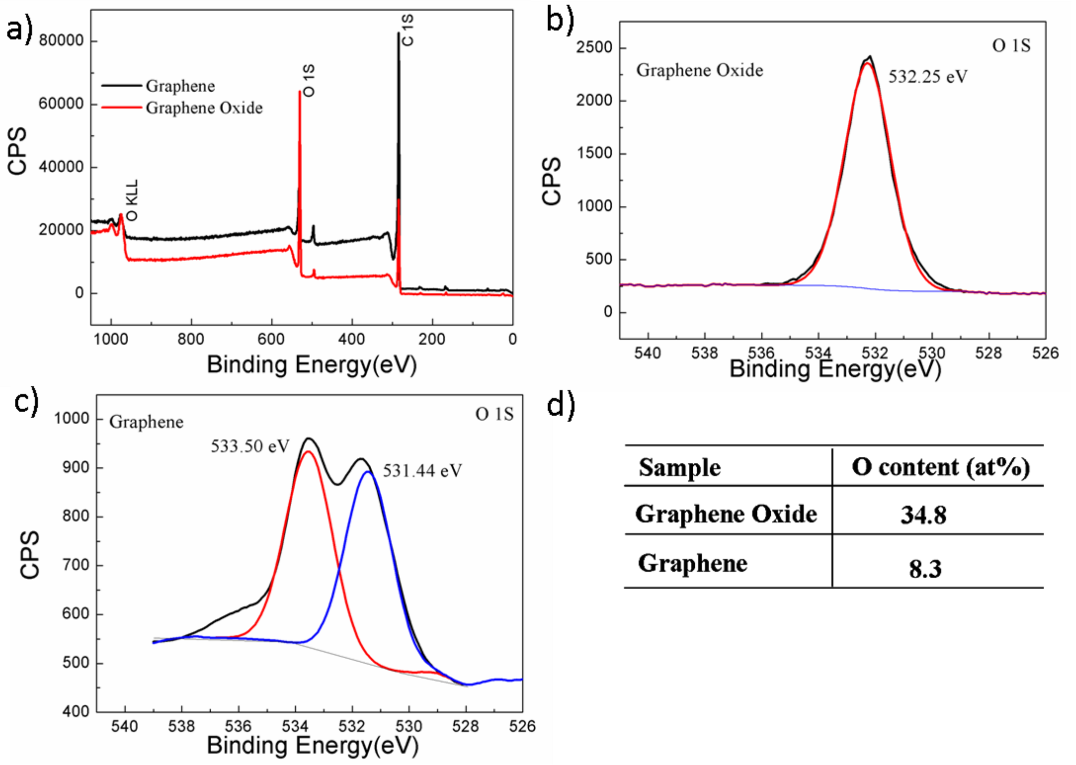
To obtain the G/SnO_2 NR/C hierarchical structures, 20 mg of the G/SnO_2 NR samples is dispersed in 40 mL of aqueous solution of glucose (60 mg). After thorough mixing by ultrasonication for 30 minutes, the suspension is transferred into a 50 mL Teflon-lined autoclave and kept at 200 °C for 18 h. The sandwiched G/SnO_2 NR/C hybrids were collected after filtration and dried at 80 °C overnight followed by annealing at 450 °C for 2 h under Ar atomosphere.

Characterization

Products were characterized by powder X-ray diffraction (XRD, Rigaku RU-200BVH with a Co-Kα source (λ=1.7892 Å)), raman microspectroscopy (HORIBA Scientific LabRAM HR Raman spectrometer) under ambient condition with an incident laser beam at 532.03 nm, thermogravimetric analysis (TGA; Netzsch), field-emission scanning electron spectrometry (FE-SEM, Hitachi 4800S) coupled with energy dispersive spectroscopy (EDS), transmission electron microscope (TEM, Hitachi H-7000), high resolution TEM (HRTEM, JEOL 2010 FEG microscope) and X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra Al at 14 kV). The XANES experiments on the Sn M edge, O K edge and C K edge for composites were conducted on the undulator Spherical Grating Monochromator (SGM) beamline at the Canadian Light Source (CLS) located at the University of Saskatchewan in Saskatoon.[2]

Electrochemical Measurement

The working electrodes are composed of the testing materials (G/SnO_2 NR and G/SnO_2 NR/C), conductive carbon black and polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1. The coin cells (2032) were assembled using pure lithium metal foil as the counter electrode and the polypropylene as the separator inside an argon-filled glove box. The electrolyte applied was 1M $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) solvent. The profiles of galvanostatically charging and discharging curves were collected on a computer controlled Arbin BT-2000 battery tester system at a cut-off voltage window of 0.01 to 3 V (vs. Li^+/Li). Electrochemical impedance spectroscopy (EIS) measurements were conducted on an electrochemical workstation (Potentiostat/Galvanostat/EIS (VMP3)) by applying an AC voltage of 5 mV amplitude in the frequency range from 0.01 to 100 KHz at 0.5 V of specified discharged cycles. The calculation of specific capacities for G/SnO_2 NR and G/SnO_2 NR/C is based on the weight of the composites.



Sample	O content (at%)
Graphene Oxide	34.8
Graphene	8.3

Figure S1. XPS patterns of Graphene Oxide and Graphene sample: a) survey; b) O 1S of Graphene Oxide; c) O1S of Graphene; d) O content summary.

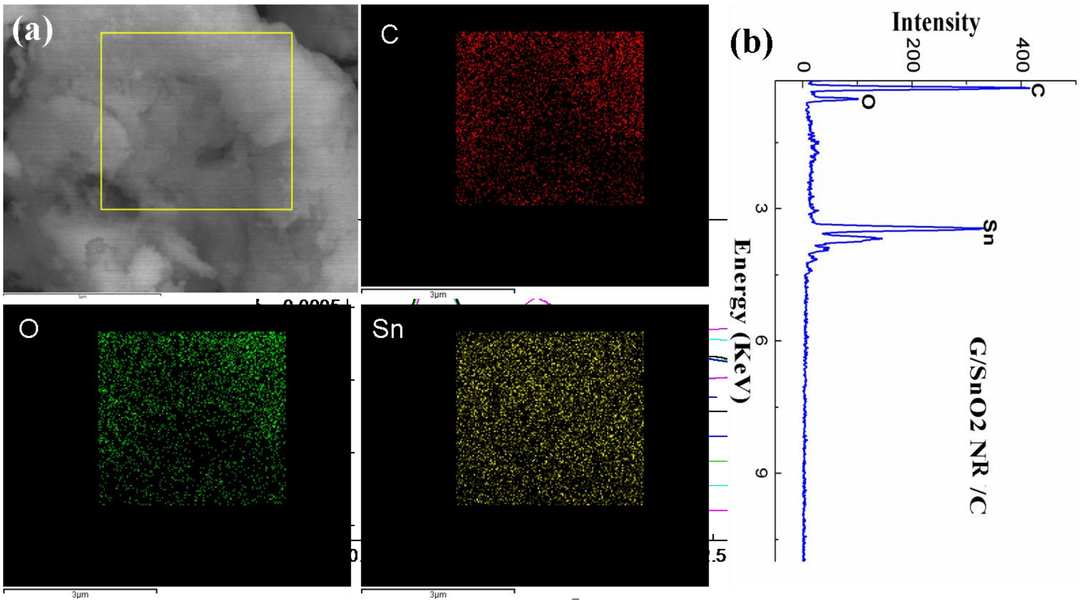


Figure S2. (a) Elemental mapping spectra and (b) energy dispersive X-ray (EDX) patterns of G/SnO_2 NR/C nanocomposites.

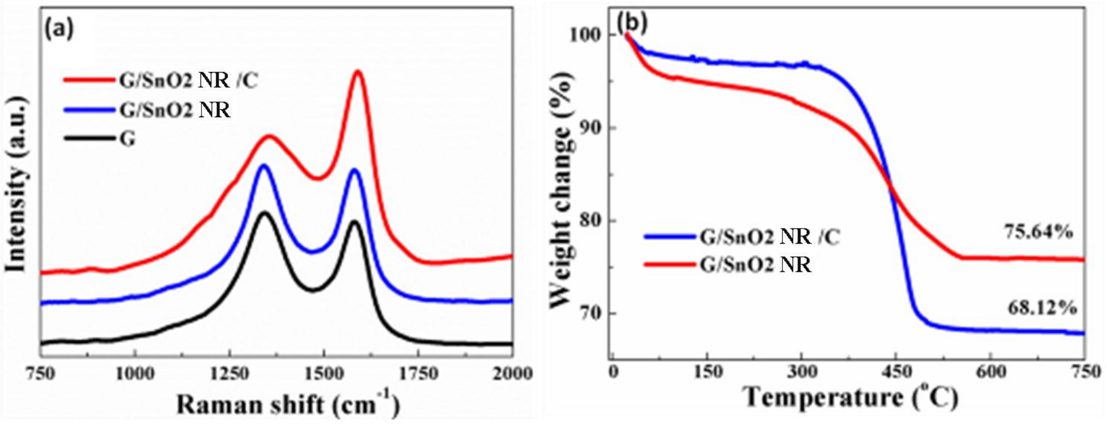


Figure S3. Characterization of G/SnO$_2$ NR and G/SnO$_2$ NR/C nanocomposites: (a) Raman spectra; (b) TGA curves.

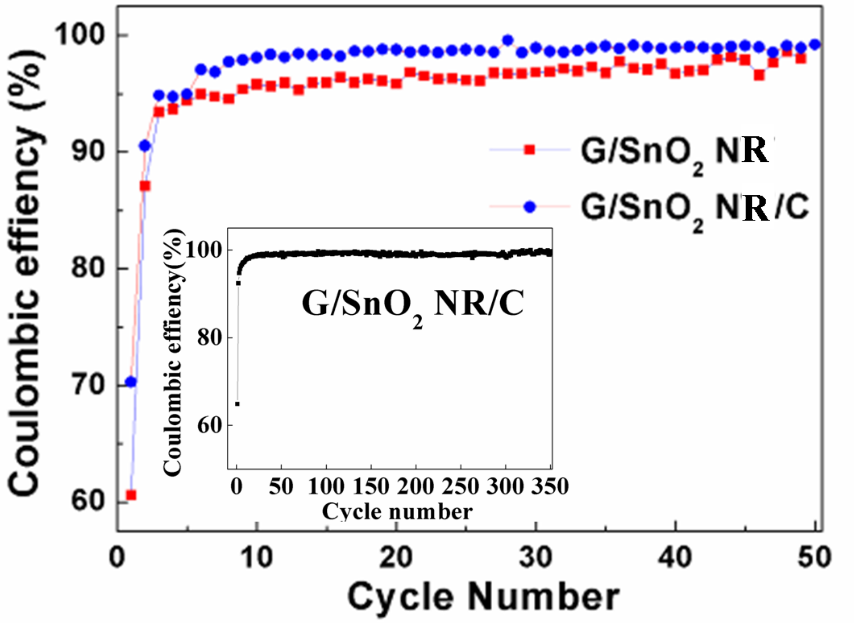


Figure S4. A comparison of Coulombic efficiency of G/SnO$_2$ NR and G/SnO$_2$ NR/C in the first 50 cycles at 0.1C (inset shows the Coulombic efficiency of G/SnO$_2$ NR/C at 1C for 350 cycles).

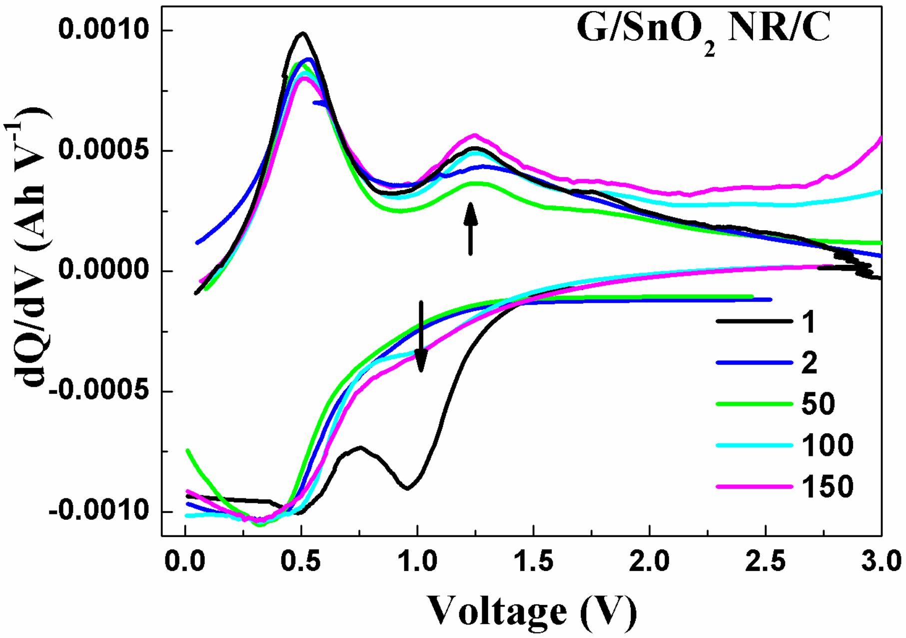


Figure S5. The differential capacity versus voltage plots of G/SnO_2 NR/C sandwiched composites at selected cycle numbers.

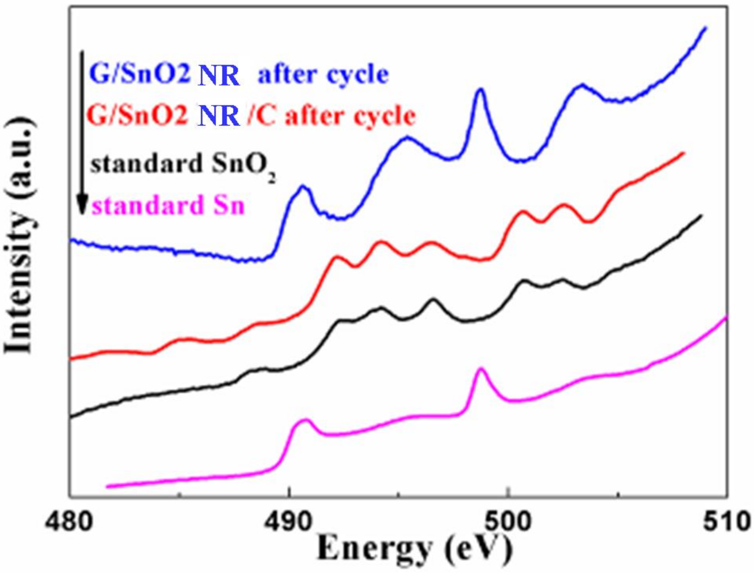


Figure S6. Sn M edge XANES spectra of standard Sn, SnO_2 and nanocomposites after cycling.

References:

1 D. Wang, X. Li, J.Wang, J. Yang, D. Geng, M.Cai, R. Li, T. K. Sham and X. Sun, *J. Phys. Chem. C*, 2012, **116**, 22149.

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