Supporting Information

Layer-by-layer self-assembly of sandwich-like graphene wrapped SnO_x@graphene composite as anode material for lithium ion batteries

Jingjing Tang,[a] Juan Yang,[a] Limin Zhou,[b] Jing Xie,[a] Guanghui Chen,[a] and Xiangyang Zhou*[a]

[a]*School of Metallurgical Science and Engineering, Central South University,*

Changsha, 410083, China

[b]*Department of Mechanical and Engineering, The Hong Kong Polytechnic University,*

Hong Kong, China

*Corresponding author. E-mail: hncsyjy308@163.com

Experimental section

Materials and Reagents:

Graphite powder (purity>99.99%), Sulfuric acid (95-98%, AR grade), sodium nitrate (AR grade), potassium permanganate (AR grade), hydrogen peroxide (30%, AR grade), hydrochloric acid (36-38%, AR grade), ammonium hydroxide (25-28%, AR grade), hydrazine (80%, AR grade), $SnCl_2 \cdot 2H_2O$ (AR grade), polydiallydimethylammonium chloride (PDDA, average Mw=100,000~200,000, 20 wt% in water, Aldrich). All reagents are used as received.

Material Synthesis:

Synthesis of graphene oxide (GO). Graphite oxide was synthesized from graphite powder based on modified Hummer's method [1]. Typically, under magnetic stirring

in a ice bath, 1 g of $NaNO_3$ and 1 g of graphite powder were put into cold concentrated H_2SO_4 (50 ml). Then 5 g of $KMnO_4$ was added gradually under stirring. The ice bath reaction was allowed to continue for 4 h. Then, the mixture was stirred at 35 ℃ for 4 h. Then deionized water (100 ml) was gradually added under extensive stirring to keep the temperature below 70 ℃. The temperature of the water bath was increased to 90 ℃ and maintained for 2 h to increase the degree of oxidation of the product. The obtained bright yellow suspension was diluted with deionized water (100 ml) and further treated with 5 ml of H_2O_2 to reduce the residual $KMnO_4$. Finally, graphite oxide was obtained by centrifugation with diluted HCl and abundant deionized water. As-prepared graphite oxide was dispersed in deionized water by ultrasonication for 2 h to get the homogeneous GO aqueous with a concentration of 0.2 mg ml^{-1} to be used.

Synthesis of SnO$_2$@G. After the dissolution of $SnCl_2 \cdot 2H_2O$ (2 g) in GO dispersion, the mixture was magnetically stirred at 90 ℃ for 0.5 h. And then ammonia was added drop by drop to adjust the pH value of the dispersion to neutral to get SnO$_2$@GO. The resulting black filter cake was dissolved in deionized water after vacuum filtration and washing. After the addition of 5 ml of $NH_3 \cdot H_2O$ and 0.2 ml of $N_2H_4 \cdot H_2O$, the mixture was further stirred for 2 h at 95 ℃. SnO$_2$@G was collected as black precipitate, washed several times with deionized water and dried.

Synthesis of SnO$_x$@G/G. After the dissolution of $SnCl_2 \cdot 2H_2O$ (2 g) in GO dispersion, the mixture was magnetically stirred at 90 ℃ for 0.5 h. And then ammonia was added drop by drop to adjust the pH value of the dispersion to neutral to get

SnO$_2$@GO. The resulting black filter cake was dissolved in deionized water after vacuum filtration and washing. To prepare positively charged SnO$_2$@GO (p-SnO$_2$@GO), 2 ml of PDDA (polydiallydimethylammonium chloride, average Mw=100,000~200,000, 20 wt% in water, Aldrich) was transferred into SnO$_2$@GO solution and stirred for 10 h. p-SnO$_2$@GO was obtained after vacuum filtration and washing. Subsequently, p-SnO$_2$@GO was dispersed into homogeneous GO aqueous and the mixture was stirred for 2 h. After the addition of 5 ml of NH$_3$•H$_2$O and 0.2 ml of N$_2$H$_4$•H$_2$O, the mixture was further stirred for 2 h at 95 ℃. Sandwich-like SnO$_x$@G/G was collected as black precipitate, washed several times with deionized water and dried.

Characterization:

Scanning electron microscopy (QUANTA FEG 250, AMERICA) and transmission electron microscopy (TEM, Titan G2 60-300, HOLLAND) were used to characterize the materials. Thermo-gravimetric analysis (TGA) was conducted with a heating rate of 10 ℃ min^{-1} using a SDTQ600 in air. The crystal structures of samples were measured by X-ray powder diffraction (XRD, Rigaku-TTRIII, Cu Kα) at a scanning rate of 10° min^{-1}. X-ray photoelectron spectra (XPS) were recorded using an X-ray photoelectron spectrometer (K-Alpha 1063) with a monochromatic Al Kα X-ray source. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer.

Electrochemical measurement:

Working electrodes were fabricated by mixing the synthesized samples, acetylene

carbon black and polyvinylidene fluoride (PVDF) binder dissolved in N-methyl-2-pyrrolidone (NMP) at a weight ratio of 80:10:10. The mixed slurry was then coated onto a copper foil and dried overnight at 120 ℃ in a vacuum oven prior to assembling the customized test cell, which employed a lithium foil as the counter electrode and 1M $LiPF_6$ in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1:1:1) as the electrolyte. Cells were assembled in an ultra pure argon filled glove box (Super 1220/750, Shanghai Mikrouna Co. Ltd). Galvanostatic discharging/charging was carried out on a LAND CCT-2001A in the potential range 0.005-3 V versus Li/Li^+ at a certain current density value. Cyclic voltammograms (CV) experiment was performed on an electrochemical workstation (CHI660E) over the potential range 0.005-3 V versus Li/Li^+ at a scanning rate of 0.5 mV s^{-1}.

Table S1 Comparison of the electrochemical performance of SnO$_x$/graphene based on previous literatures.

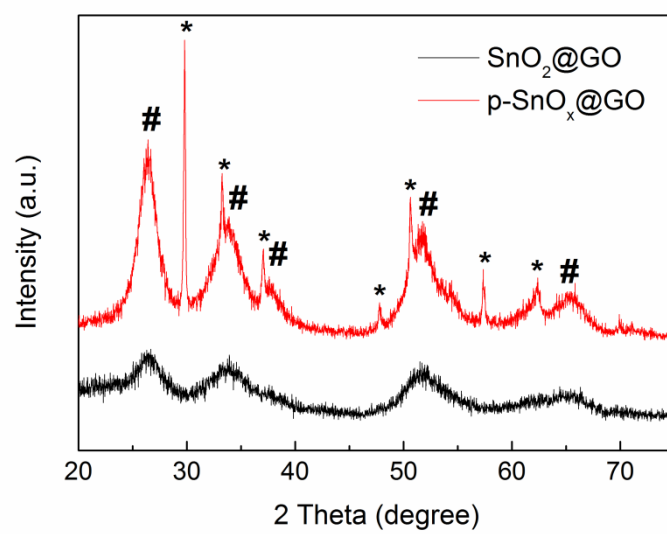| Sample	The content of SnO$_x$	Electrochemical data						Ref. No.
		Current density / mA g^{-1}	Potential range / V	Initial discharge capacity / mAh g^{-1}	Initial charge capacity / mAh g^{-1}	Reversible capacity after 50 cycles / mAh g^{-1}	Reversible capacity after 100 cycles / mAh g^{-1}	
SnO$_2$/G	75.64%	100	0.01-3.00	1870	1133	389	-	[2]
SnO$_2$/G/C	68.12%	100	0.01-3.00	1828	1285	~700	~630	[2]
SnO/SnO$_2$/G	~95%	100	0.0-2.0	1343	575.9	-	-	[3]
SnO$_2$@G@G	90%	80	0.01-2.00	1705.5	1050.6	-	~590	[4]
SnO2/G	~68%	100	0.01-2.0	1662	819	-	~600	[5]
SnO2/G	-	100	0.0-3.0	-	1306	594	-	[6]
SnO$_2$/G	~78%	78.2	0.01-3	1526.9	977.2	~507.9	-	[7]
SnO$_2$/G	-	50	0.05-3	~1400	~975	~975	-	[8]

Fig. S1 XRD pattern of SnO$_2$@GO and p-SnO$_x$@GO.
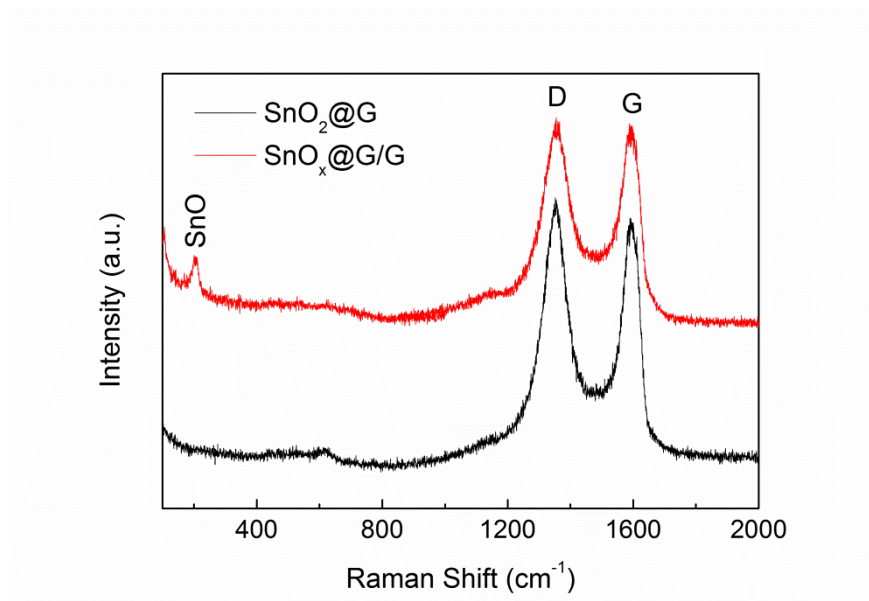
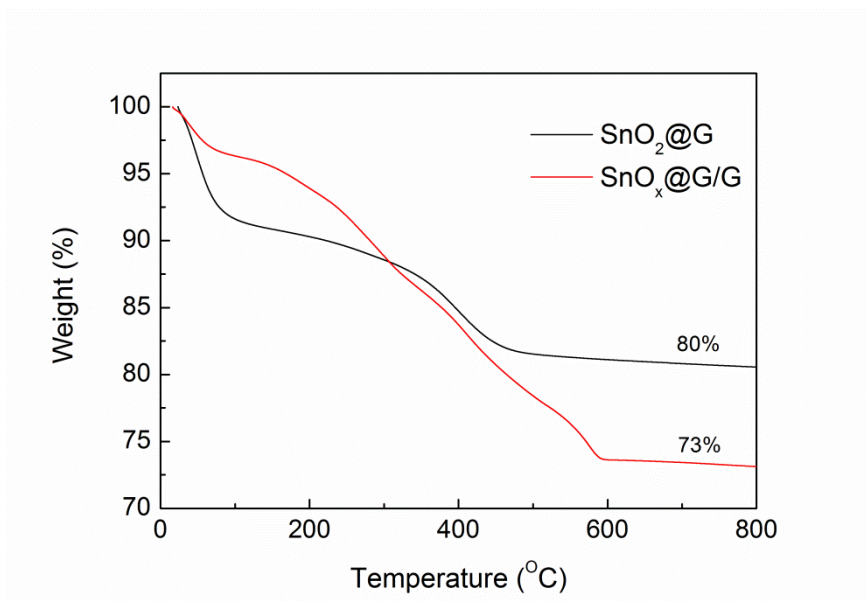**Fig. S2** Raman spectra of $SnO_2@G$ and $SnO_x@G/G$.

Fig. S3 TGA curves of HCl washed-SnO$_x$@G/G and SnO$_2$@G under air atmosphere
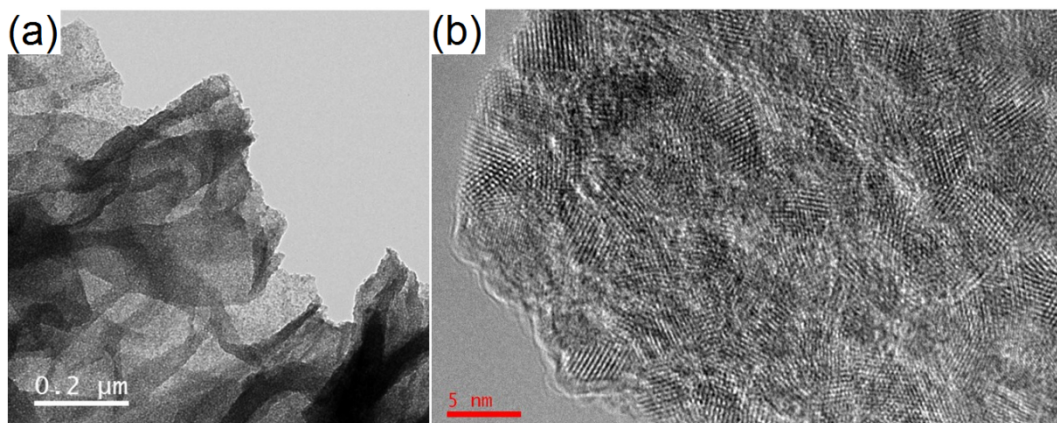
at a heating rate of 5 ℃ min^{-1}.

Fig. S4 TEM images of SnO$_2$@G.

References

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

[2] D. Wang, J. Yang, X. Li, D. Geng, R. Li, M. Cai, T. Sham and X. Sun, *Energy Environ. Sci.*, 2013, **6**, 2900-2906.

[3] X. Chen, K. Wang, Y. Zhai, H. Zhang, X. Wu, X. Wei and J. Chen, *Dalton Trans.*, 2014, **43**, 3137-3143.

[4] J. Zhu, G. Zhang, X. Yu, Q. Li, B. Lu and Z. Xu, *Nano Energy*, 2014, **3**, 80-87.

[5] S. K. Park, S. Yu, N. Pinna, S. Woo, B. Jang, Y. Chung, Y. Cho, Y. Sung and Y. Piao, *J. Mater. Chem.*, 2012, **22**, 2520-2525.

[6] J. Liu, J. Huang, L. Hao, H. Liu and X. Li, *Ceram. Int.*, 2013, 8623-8627.

[7] S. Yang, W. Yue, J. Zhu, Y. Ren and X. Yang, *Adv. Funct. Mater.*, 2013, **23**, 3570-3576.

[8] X. Wang, X. Cao, L. Bourgeois, H. Guan, S. Chen, Y. Zhong, D. Tang, H. Li, T. Zhai, L. Li, Y. Bando and D. Golberg, *Adv. Funct. Mater.*, 2012, **22**, 2682-2690.