Conformal Graphene Encapsulation of Tin Oxide Nanoparticle Aggregates for Improved Performance in Reversible Li^+ Storage

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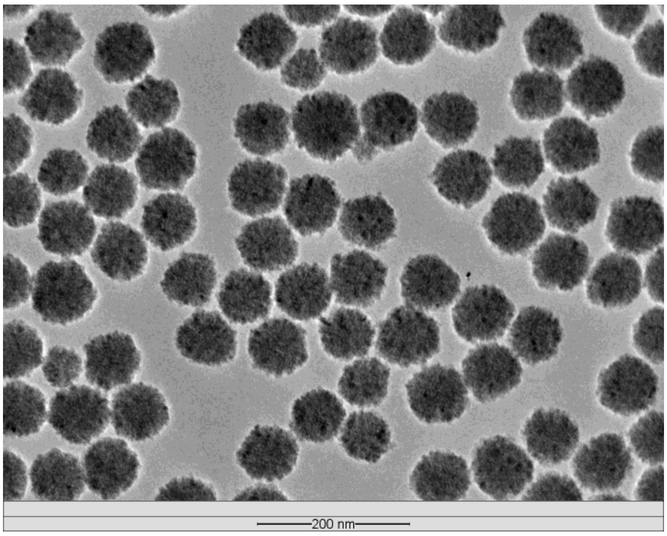

Fig. S1 TEM image of hydrothermally synthesized SnO_2 coated with a thin layer of glucose-derived, carbon-rich polysaccharides.

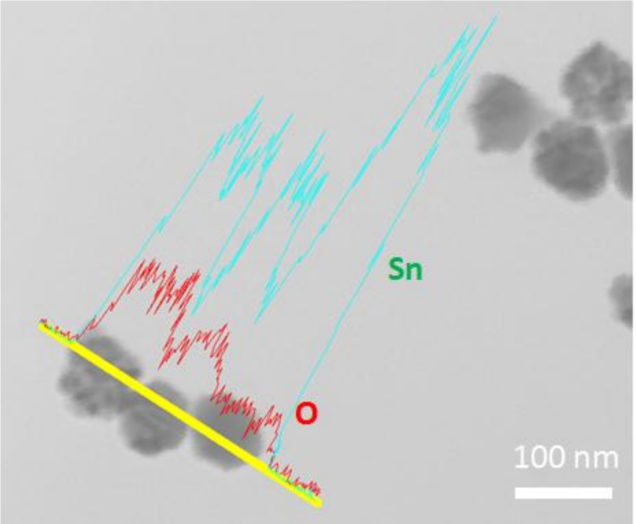

Fig. S2 Linescan image of three representative SnO_2@TRGO-5 particles.

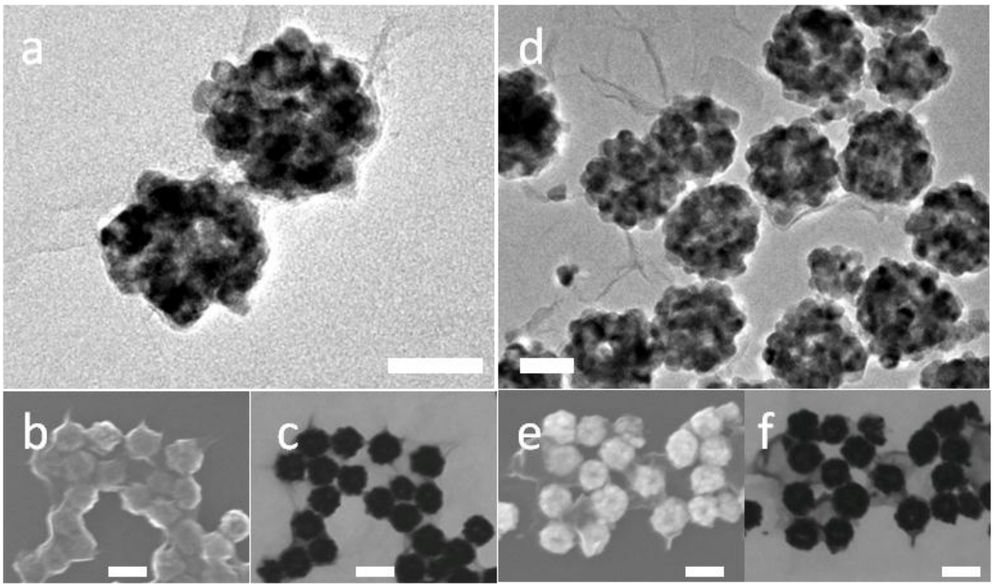

Fig. S3 Morphology of intermediate and final products in the graphene encapsulation of SnO_2 NP aggregates. a, d) TEM, b, e) FESEM and c, f) STEM images of a-c) SnO_2@GO-10 and h-j) SnO_2@TRGO-10. All scale bars are 100 nm in length.

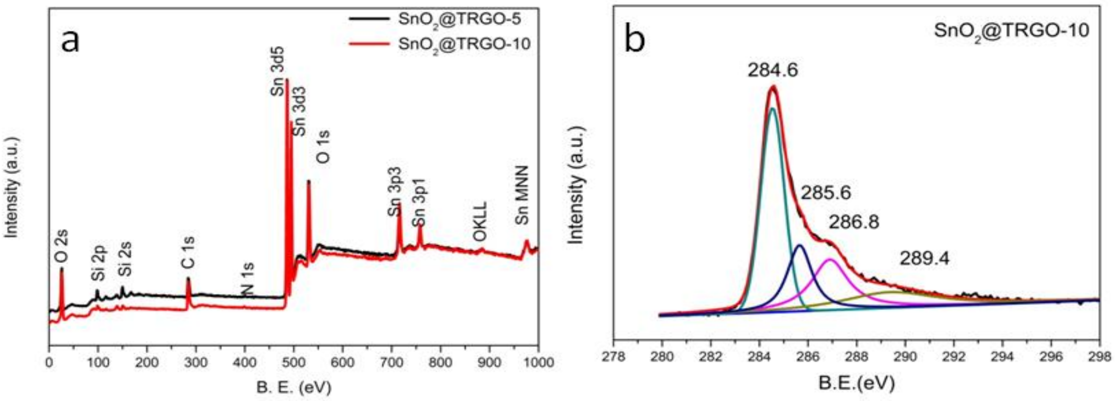

Fig. S4 a) XPS survey scan spectra of SnO_2@TRGO-5 and SnO_2@TRGO-10, b) C1s XPS spectrum of SnO_2@TRGO-10.

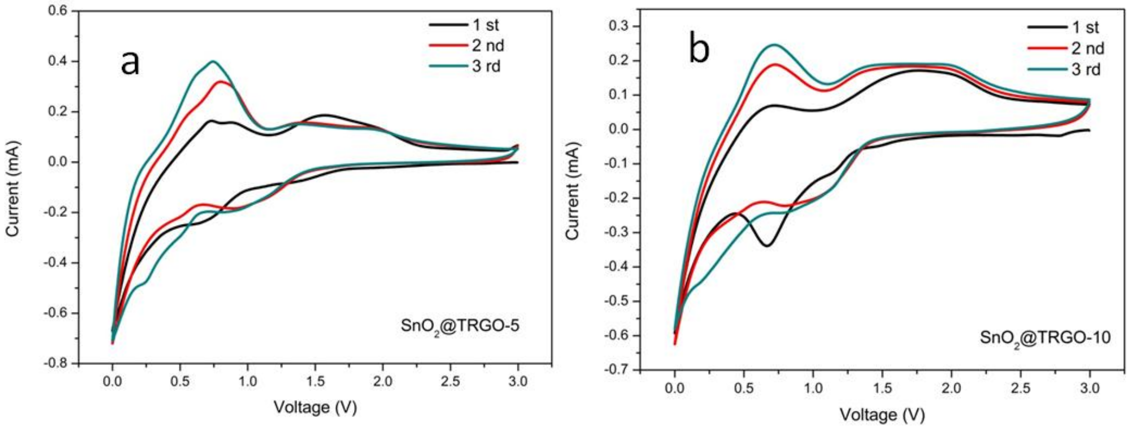

Fig. S5 Cyclic voltammograms of a) SnO_2@TRGO-5 and b) SnO_2@TRGO-10 at 0.2 mV/s in the $0-3$ V *vs.* Li^+/Li voltage window.

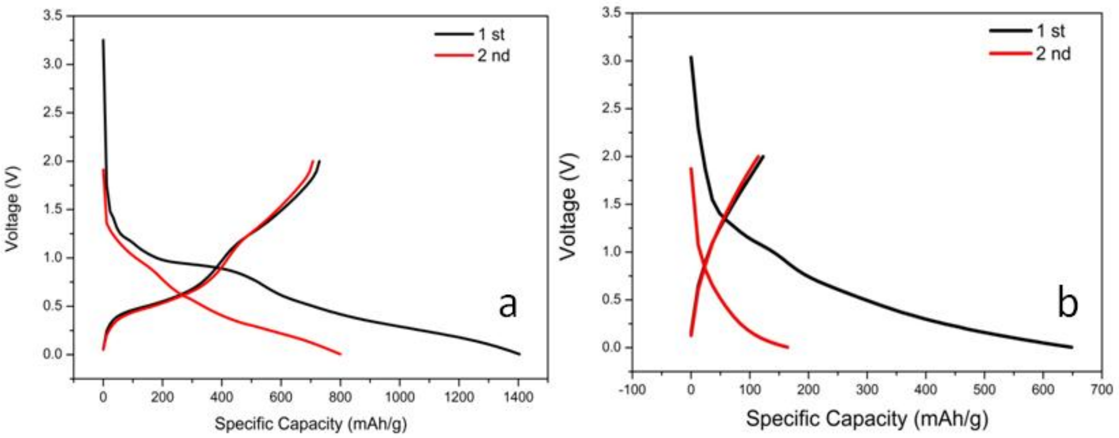

Fig. S6 Discharge and charge curves of a) SnO$_2$, b) TRGO at 200 mA/g in the 0.005 − 2 V *vs*. Li voltage window.

Analysis of ICL:
From the first 2 cycle discharge/charge curves of tin oxide (Fig. S6a) and TRGO (Fig. S6b), the first cycle discharge and charge capacities of tin oxide were 1394.3 and 723.7 mAh/g respectively resulting in a first cycle ICL of 47.8 %. This ICL was caused by tin oxide reduction to tin as well as SEI formation.[1] The ICL related to the former could be estimated from the capacity in the 1.0 − 0.8 V voltage window of the discharge curve of pristine tin oxide in Fig. S5a. The value calculated as such was 300 mAh/g. The ICL due to SEI formation could then be calculated as the difference between the measured ICL and the ICL due to tin oxide reduction. For pristine tin oxide this value was 371 mAh/g. The first cycle discharge and charge capacities of TRGO were 648.2 and 122.7 mAh/g. The large ICL of 81.1% is typical for the graphene anodes in lithium ion batteries.[2-3] An earlier report has attributed this to lithium interactions with the residual oxygen-containing functional groups within the graphene sheet, SEI formation and the barrier in Li$^+$ diffusion out of a well-ordered graphene structure.[4] The first cycle discharge and charge capacities calculated from the discharge/charge curves in Fig. 5a were 1326.1 and 749.9 mAh/g (or ICL of 43.4%) for SnO$_2$@TRGO-5; and 1141.2 and 435.0 mAh/g (or ICL of 61.9%) for SnO$_2$@TRGO-10. Assuming the ICL caused by tin oxide reduction remained the same as 300 mAh/g for tin oxide in the SnO$_2$@TRGO composites, the ICL corresponding to the reduction of tin oxide to tin in SnO$_2$@TRGO-5 was calculated to be 300 mAh/g × (1 − 0.05 − 0.21) = 222 mAh/g, while the corresponding value for SnO$_2$@TRGO-10 was 300 mAh/g × (1 − 0.09) = 273 mAh/g. The ICL contributed by the graphene shell on the tin oxide surface was calculated to be 354.2 mAh/g for SnO$_2$@TRGO-5 and 433.2 mAh/g for SnO$_2$@TRGO-10 respectively. Since SEI formation should occur to the same extent on these two SnO$_2$@TRGO composites due to the compactness of the graphene shell, their difference (79 mAh/g) in ICL could be attributed to a greater content of residual oxygen-containing functional groups and/or the difficulty of Li$^+$ diffusion in SnO$_2$@TRGO-10. The discharge capacity of SnO$_2$@TRGO-10 in the first cycle was also smaller than SnO$_2$@TRGO-5, suggesting that the ICL difference was mainly caused by the greater difficulty of Li$^+$ diffusion in SnO$_2$@TRGO-10.

Table S1 Comparison of the electrochemical performance of tin oxide/graphene composites

Reference	***Graphene content***	***Carbon additive***	***Voltage window***	***Cyclability*** *(current density;* *Reported lithiation capacity)*
Paek, S. M., E. Yoo, et al. (2009), Nano Letters 9(1): 72-75.	*40 wt%*	*None*	*0.05-2 V*	*50 mA/g;* *570 mAh/g after 30 cycles*
Li, Y., X. Lv, et al. (2010). The Journal of Physical Chemistry C 114(49):21770-21774.	*26 wt%*	*15 wt%*	*0.01-1.5 V*	*200 mA/g;* *377 mAh/g after 35 cycles*
Ding, S., D. Luan, et al. (2011). Chemical Communications 47(25): 7155-7157.	*18 wt%*	*20 wt%*	*0.01-1.2 V*	*400 mA/g;* *518 mAh/g after 50 cycles*
Huang, X., X. Zhou, et al. (2011). Chemphyschem 12(2): 278-281.	*22.5 wt%*	*None*	*0-2 V*	*50 mA/g;* *510 mA/g after 20 cycles*
Liang, R., H. Cao, et al. (2011). Journal of Materials Chemistry 21(44): 17654-17657.	*2.3 wt%*	*11.3 wt%* *PANI*	*0.01-3 V*	*200 mA/g;* *574 mAh/g after 50 cycles* ** 440 mAh/g (0-2 V) after 50 cycles*
Zhang, M., D. Lei, et al. (2011). Journal of Materials Chemistry 21(6): 1673-1676.	*15 wt%*	*10 wt%*	*0.005-2V*	*0.2 C(120 mA/g);* *600 mAh/g after 50 cycles*
Zhong, et al. (2011). The Journal of Physical Chemistry C.	*33.3 wt%*	*10 wt%*	*0-3 V*	*100 mA/g;* *604 mAh/g after 50 cycles* ** 460 mAh/g (0-2 V)after50 cycles*
Li, B., H. Cao, et al. (2012) Journal of Materials Chemistry 22(7): 2851-2854.	*20 wt%*	*None*	*0.001-3V*	*200 mA/g;* *700 mAh/g after 50*

				cycles ** 430 mAh/g after 50 cycles*
Park, S.-K., S.-H. Yu, et al. (2012). Journal of Materials Chemistry 22(6): 2520-2525.	*30 wt%*	*15 wt%*	*0.01-2 V*	*100 mA/g;* *626 mAh/g after 50 cycles*
SnO_2@TRGO-5	*5 wt%*	*None*	*0.005-2 V*	*100 mA/g;* *700 mAh/g after 30 cycles*
SnO_2@TRGO-5	*5 wt%*	*None*	*0.005-2 V*	*200 mA/g;* *517 mAh/g after 50 cycles*

Notes: This paper uses the the weight of the whole electrode for the calculation of specific capacities. In most of the published papers, the calculation was based on the weight of tin oxide only. We cited those values in verbatim without re-nomalization. However, charge capacities tested in the 0-3V region were re-normlized to the 0-2 V window based on the charge-discharge curves in those reports.

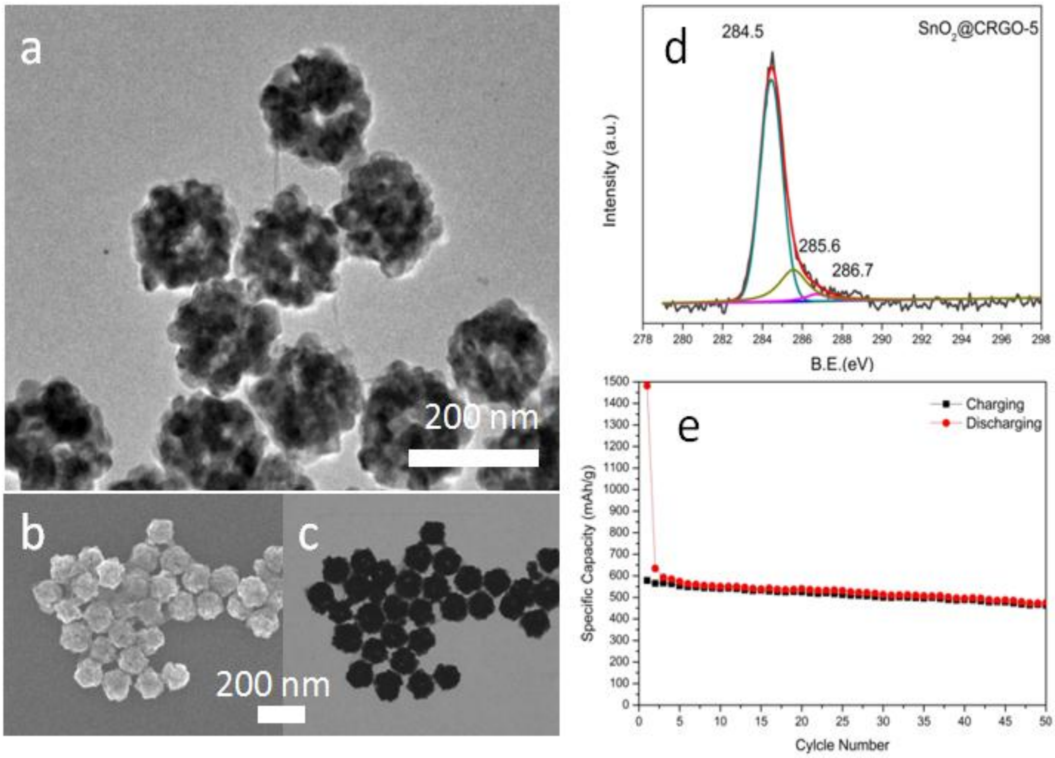

Fig. S7 a) TEM, b) FESEM and c) STEM images, d) C1s XPS spectrum and e) cycle stability of SnO_2@CRGO-5. SnO_2@CRGO-5 was prepared by followed procedure: 50 mg

SnO_2@GO-5 was dispersed in 10 mL hydrazine (N_2H_4, 53%) for 0.5 h with stirring. The recovered solid was washed by DI water for 3 times.

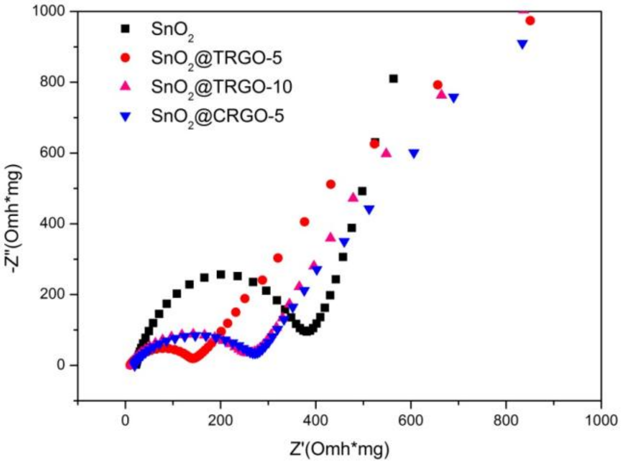

Fig. S8 Nyquist plots of SnO_2, SnO_2@TRGO-5, SnO_2@CRGO-5 and SnO_2@TRGO-10 electrodes before cycling at a discharged potential of 1.6 V (*vs.* Li/Li^+) in the 100 kHz to 0.1 Hz frequency region.

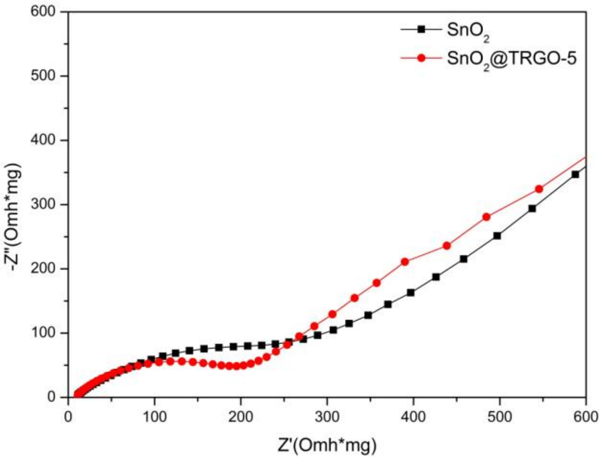

Fig. S9 Nyquist plots of SnO_2, SnO_2@TRGO-5 after 50 discharge/charge cycles at a discharged potential of 1.6 V (*vs.* Li/Li^+). Frequency range: 100 kHz to 0.1 Hz.

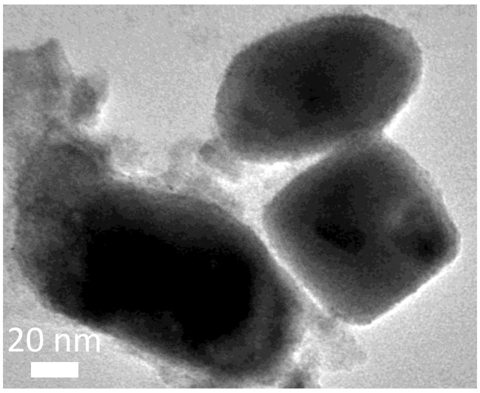

Fig. S10 TEM image of SnO_2@TRGO-5 after 50 cycles.

References

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