



Short communication

## Reduced graphene oxide/tin oxide composite as an enhanced anode material for lithium ion batteries prepared by homogenous coprecipitation

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## ABSTRACT

Reduced graphene oxide/tin oxide composite is prepared by homogenous coprecipitation. Characterizations show that tin oxide particles are anchored uniformly on the surface of reduced graphene oxide platelets. As an anode material for Li ion batteries, it has 2140 mAh g<sup>-1</sup> and 1080 mAh g<sup>-1</sup> capacities for the first discharge and charge, respectively, which is more than the theoretical capacity of tin oxide, and has good capacity retention with a capacity of 649 mAh g<sup>-1</sup> after 30 cycles. The simple synthesis method can be readily adapted to prepare other composites containing reduced graphene oxide as a conducting additive that, in addition to supporting metal oxide nanoparticles, can also provide additional Li binding sites to, perhaps, further enhance capacity.

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## 1. Introduction

Lithium ion batteries are the favored power sources for portable electronic devices such as laptop computers, cellular phones, camcorders, and mp3 players. Graphite is a standard anode material in Li-ion batteries as lithium can insert and deinsert during discharging and charging, respectively, with a theoretical specific capacity of 372 mAh g<sup>-1</sup> [1]. However, in order to meet the increasing demand for batteries with higher energy densities, it is essential to develop electrodes made from durable, nontoxic, and inexpensive materials with a high charge/discharge rate and a higher reversible capacity. Tin and tin oxides, which have higher theoretical capacities (Sn: 994 mAh g<sup>-1</sup>, and SnO<sub>2</sub>: 782 mAh g<sup>-1</sup>) compared to graphite, have been proposed as alternative anode materials [2–4]. However, the practical application of tin oxide as an anode is hampered by its poor cyclability, resulting from large volume changes of over 300% during discharge/charge, leading to electrical disconnection from the current collector [5–7]. One approach to circumvent this limitation is to hybridize SnO<sub>2</sub> with carbonaceous materials to better accommodate the strain during volume change [8,9]. On the other hand, graphene has excellent electronic conductivity, high theoretical surface area of 2630 m<sup>2</sup> g<sup>-1</sup>, good mechanical properties, and can be used as a conducting additive for hybrid nanostructured materials [10–14]. Recently, high surface area chemically modified graphene has been used to form hybrid materials with SnO<sub>2</sub>, TiO<sub>2</sub>

and Mn<sub>3</sub>O<sub>4</sub> nanoparticles with the aim of improving the capacity and cycling stability of the resulting electrode materials [15–17]; it is a challenge to find a good method to prepare reduced graphene oxide (RG-O) and metal oxide composite, resulting in the homogeneous dispersion of metal oxide nanoparticles on the 'graphene' matrix.

We report here a simple method for obtaining RG-O–SnO<sub>2</sub> composite by (i) homogeneous precipitation of SnCl<sub>4</sub> in a suspension of graphene oxide (G-O) platelets using urea and (ii) subsequent reduction of the G-O with hydrazine under microwave irradiation to yield RG-O platelets decorated with SnO<sub>2</sub> nanoparticles, and finally (iii) annealing at 500 °C for 3 h under a nitrogen atmosphere with the aim of increasing crystallinity of the SnO<sub>2</sub> nanoparticles. As an anode material for Li-ion batteries, the RG-O/SnO<sub>2</sub> composite exhibited unprecedentedly high discharge and charge capacities of 2140 and 1080 mAh g<sup>-1</sup>, respectively, for the first cycle, normalized to the mass of SnO<sub>2</sub> in the composite (~1712 and 864 mAh g<sup>-1</sup> respectively, based on the total mass of the composite), and good cycling performance with 649 mAh g<sup>-1</sup> capacity at the 30th discharge. Our method of synthesis presents a promising route for large scale production of RG-O platelet/metal oxide nanoparticle composites as electrode materials for Li ion batteries.

## 2. Experimental

## 2.1. Synthesis of graphite oxide

Graphite oxide was synthesized from natural graphite by a modified Hummers method. Briefly, graphite powders (2 g; SP-1, Bay

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Carbon, MI) and  $\text{NaNO}_3$  (1 g; Aldrich, >99%) were mixed, then put into concentrated  $\text{H}_2\text{SO}_4$  (96 ml; Fisher Scientific, 98%) in an ice bath. Under vigorous stirring,  $\text{KMnO}_4$  (6 g; Fisher Scientific, 99.6%) was gradually added and the temperature of the mixture was kept below  $20^\circ\text{C}$ . After removing the ice bath, the mixture was stirred at  $35^\circ\text{C}$  in a water bath for 18 h. As the reaction progressed, the mixture became pasty with a brownish color. 150 ml  $\text{H}_2\text{O}$  was then slowly added to the pasty mixture. Addition of water into the concentrated  $\text{H}_2\text{SO}_4$  medium generates large amounts of heat; therefore water should be added slowly and while keeping the mixture in an ice bath to maintain the temperature below  $50^\circ\text{C}$ . After dilution with 240 ml  $\text{H}_2\text{O}$ , 5 ml of 30%  $\text{H}_2\text{O}_2$  (Fisher Scientific) was added to the mixture, and the color of this diluted solution became a brilliant yellow. After continuously stirring for 2 h, the mixture was filtered and washed with 10%  $\text{HCl}$  (aq) (250 ml; Fisher Scientific), then DI water and then ethanol (Fisher Scientific, anhydrous) to remove other ions [18]. Finally, the resulting solid was dried under vacuum.

### 2.2. Preparation of reduced graphene oxide– $\text{SnO}_2$ composite (RG-O/ $\text{SnO}_2$ )

The RG-O/ $\text{SnO}_2$  composite was prepared by homogeneous precipitation with urea and subsequent reduction with hydrazine under microwave irradiation. In a typical experiment, 1 mmol  $\text{SnCl}_4 \cdot 6\text{H}_2\text{O}$  (0.36 g; Fisher Scientific, 98%) and 2 mmol urea (1.20 g; Aldrich, 98%) were separately dissolved in 25 ml water. Then these urea and  $\text{SnCl}_4$  solutions were slowly and sequentially added to 50 ml of graphite oxide suspension ( $2 \text{ mg ml}^{-1}$ ) under stirring, respectively. After exposure to ultrasound from an ultrasonic bath (VWR, B2500A-MT) for 30 min, the mixture was put in a microwave oven (Sensor Microwave Oven, DE68-00307A) and irradiated for 60 s. When cooling to ambient temperature, 0.5 ml  $\text{N}_2\text{H}_4$  (Aldrich, 64–65%) was added to the mixture while it was being continuously stirred. After that, the mixture was then put into the microwave oven and irradiated for an additional 60 s. The mixture color changed from black-brown to black. Once the reaction was completed, the product was collected by filtration. The as-prepared product was washed several times with DI water to remove the excess hydrazine as well as other ions. In order to obtain good crystallinity, the product was annealed at  $500^\circ\text{C}$  for 3 h in a tube furnace under an atmosphere of nitrogen. For comparison,  $\text{SnO}_2$  without RG-O was also synthesized using the same process.

### 2.3. Characterization

The structure of the obtained RG-O/ $\text{SnO}_2$  composite was characterized by X-ray diffraction (XRD) (X'pert, Philips) using  $\text{CuK}\alpha$  radiation. SEM investigations were performed using an FEI Quanta-600 FEG Environmental SEM. Micro Raman measurements were carried out using a WiTec Alpha 300 system with a 532-nm wavelength incident laser light. Thermal gravimetric analysis (TGA) was done with a Perkin-Elmer TGA 4000 using a heating rate of  $5^\circ\text{C min}^{-1}$  under  $20 \text{ ml min}^{-1}$  air flow. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos AXIS Ultra DLD XPS equipped with a  $180^\circ$  hemispherical energy analyzer to characterize the particles' surface. Photoemission was stimulated by monochromated  $\text{Al K}\alpha$  radiation (1486.6 eV) with an operating power of 150 W. It was operated in the analyzer mode at 80 eV for survey scans and 20 eV for detailed scans of core level lines. Binding energies were referenced to the C 1 s binding energy set at 284.5 eV.

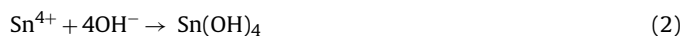
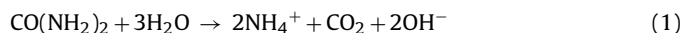
### 2.4. Electrochemical characterization

Electrochemical experiments were performed using 2032 coin-type cells. The working electrode consisted of 95 wt% active

material and 5 wt% polytetrafluoroethylene binder. The electrolyte was a solution of 1 M  $\text{LiPF}_6$  in EC/DEC (1:1 by volume) (purchased from Novolyte). Pure Li foil (Aldrich) was used as the counter electrode and the separator was Celgard 2300. The cells were discharged and charged galvanostatically for a voltage window from 0.005 to 2.0 V using a Land battery tester (China) at room temperature.

## 3. Results and discussion

As shown in Scheme 1, graphite oxide prepared by a modified Hummers method [19,20], was sonicated in water to form a suspension of G-O platelets. For the synthesis of the RG-O/ $\text{SnO}_2$  composite,  $\text{SnCl}_4$  was hydrolyzed in the G-O suspension in the presence of urea under microwave irradiation. The molar ratio of  $\text{SnCl}_4$  to urea was 1:2. This step yielded a uniform  $\text{Sn}(\text{OH})_4$  or  $\text{SnO}_2$  coating on the surface of the G-O platelets. During hydrolysis, urea releases hydroxyl ions slowly and uniformly in the suspension, resulting in the formation of  $\text{Sn}(\text{OH})_4$ , and subsequent decomposition of  $\text{Sn}(\text{OH})_4$  to  $\text{SnO}_2$  as suggested by the following reactions:

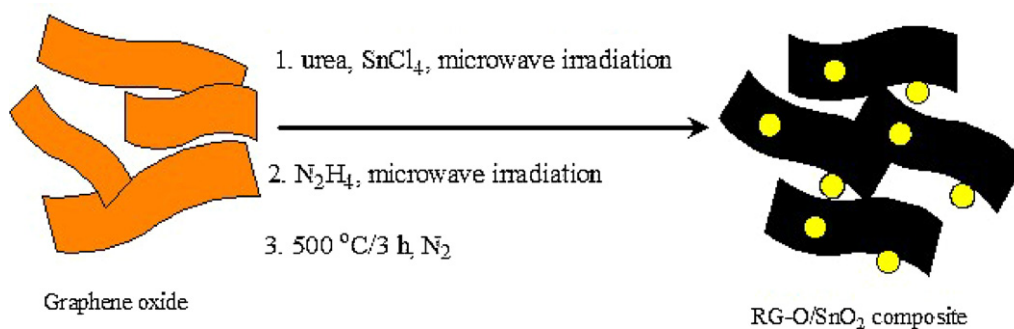


The  $\text{Sn}(\text{OH})_4$  and  $\text{SnO}_2$  particles so produced likely anchor onto the surface of the G-O platelets through oxygen-containing functional groups, such as hydroxyl, epoxy, and carboxyl.

After the suspension was cooled to room temperature, a trace of hydrazine was added to the suspension under continuous stirring and the suspension again exposed to microwave irradiation. During this process, G-O is converted into RG-O, and the  $\text{Sn}(\text{OH})_4$  decomposes to  $\text{SnO}_2$  nanoparticles as indicated in Eq. (3). The as-prepared composite obtained was characterized by XRD (see Fig. S1). The characteristic peaks of  $\text{SnO}_2$  appear but are broad and weak, indicating the  $\text{SnO}_2$  particles are amorphous and/or very small in size. In an attempt to improve the crystallinity of  $\text{SnO}_2$  particles in the composite, the product was annealed at  $500^\circ\text{C}$  for 3 h in a  $\text{N}_2$  atmosphere. XRD of the annealed composite material shows that the diffraction peaks of crystalline  $\text{SnO}_2$  nanoparticles are clearly distinguishable, and could be indexed to the tetragonal  $\text{SnO}_2$  phase (JCPDS 41-1445). The bonding nature can also be proven by the bonding states of Sn atoms as determined from Sn 3d spectrum. The Sn  $3d_{5/2}$  and  $3d_{3/2}$  spectrum is composed of single peak, respectively (see Fig. S2). And the Sn peak positions at  $\sim 487.03 \text{ eV}$  for  $3d_{5/2}$ , and at  $\sim 495.53 \text{ eV}$  for  $3d_{3/2}$  agree with the presence of  $\text{SnO}_2$  [21]. The Raman spectrum has the characteristic peaks of the tetragonal phase of  $\text{SnO}_2$  and the D and G peaks of RG-O (see Fig. S3). The composite is 20 wt% RG-O as measured by TGA (see Fig. S4).

The morphology of the as-prepared RG-O/ $\text{SnO}_2$  and RG-O/ $\text{SnO}_2$  composite was observed by scanning electron microscopy in Fig. 1. Fig. 1a and b shows that the as-prepared RG-O/ $\text{SnO}_2$  composite consists of thin, crumpled RG-O platelets closely connected with each other to form a 3D network structure. It is too small for  $\text{SnO}_2$  nanoparticles to be seen on the curved RG-O platelets. After annealing at  $500^\circ\text{C}$ , the  $\text{SnO}_2$  particle size increases to 100–200 nm in diameter, which can be seen from Fig. 1c and d. Fig. 1c and d also shows that  $\text{SnO}_2$  nanoparticles are uniformly distributed on the surface of the RG-O platelets, and can thus act as spacers to prevent the restacking of individual RG-O platelets.

To measure the performance of the RG-O/ $\text{SnO}_2$  composite as an anode for Li ion batteries, the composite was mixed with polytetrafluoroethylene (PTFE) in a weight ratio of 95:5 for preparing a working electrode, which is equivalent to a  $\text{SnO}_2$ :RG-O:PTFE ratio of 76:19:5. Despite increasing the conductivity by adding those into

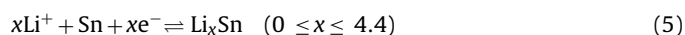
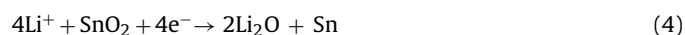


**Scheme 1.** Scheme for making RG-O/ $\text{SnO}_2$  nanoparticle composite.

the electrodes, carbon black or other conductive fillers can also lower the weight specific capacity of the electrode. In our study, carbon black (CB) was not added to the electrode, in contrast to other studies [16,17,22].

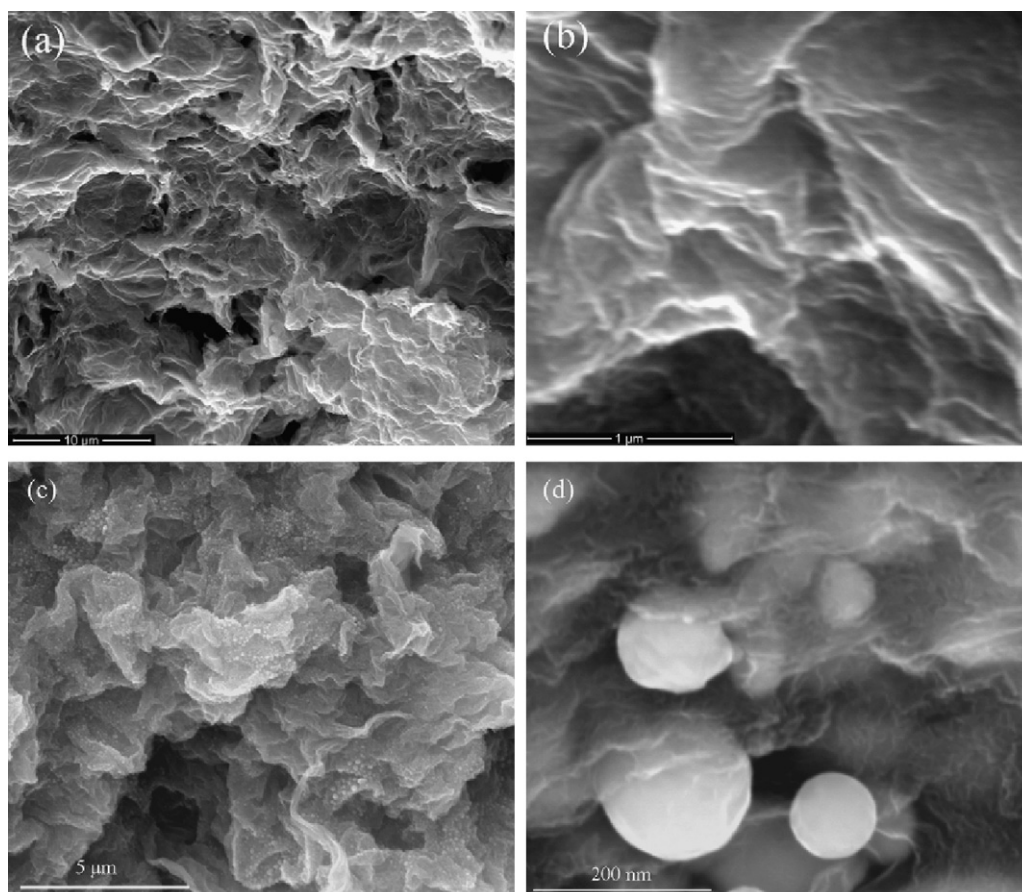
Fig. 2a shows the initial two discharge and charge curves of the RG-O/ $\text{SnO}_2$  composite at a current density of  $50\text{ mA g}^{-1}$  in a voltage range of  $2.0\text{--}0.005\text{ V}$  vs.  $\text{Li}^+/\text{Li}$ . The RG-O/ $\text{SnO}_2$  composite delivers  $2140\text{ mAh g}^{-1}$  and  $1080\text{ mAh g}^{-1}$  capacities for the first discharge and charge, respectively, based on the mass of  $\text{SnO}_2$  in the composite (The values are  $1712$  and  $864\text{ mAh g}^{-1}$ , respectively, based on the total mass of the RG-O/ $\text{SnO}_2$  composite). It can also be seen that the second discharge and charge capacities are  $1105$  and  $1009\text{ mAh g}^{-1}$ , respectively. According to Fig. 2a, the differential discharge and charge capacity of the initial two cycles vs voltage profiles of the RG-O/ $\text{SnO}_2$  composite are presented in Fig. 2b. During the first discharge, the reduction peak at  $0.95\text{ V}$  corresponds to

the formation of a solid electrolyte interface (SEI) layer and  $\text{Li}_2\text{O}$ , and disappears after the first cycle. The reduction peak at  $0.24\text{ V}$  corresponds to the formation of  $\text{Li}_x\text{Sn}$  alloys [21]:

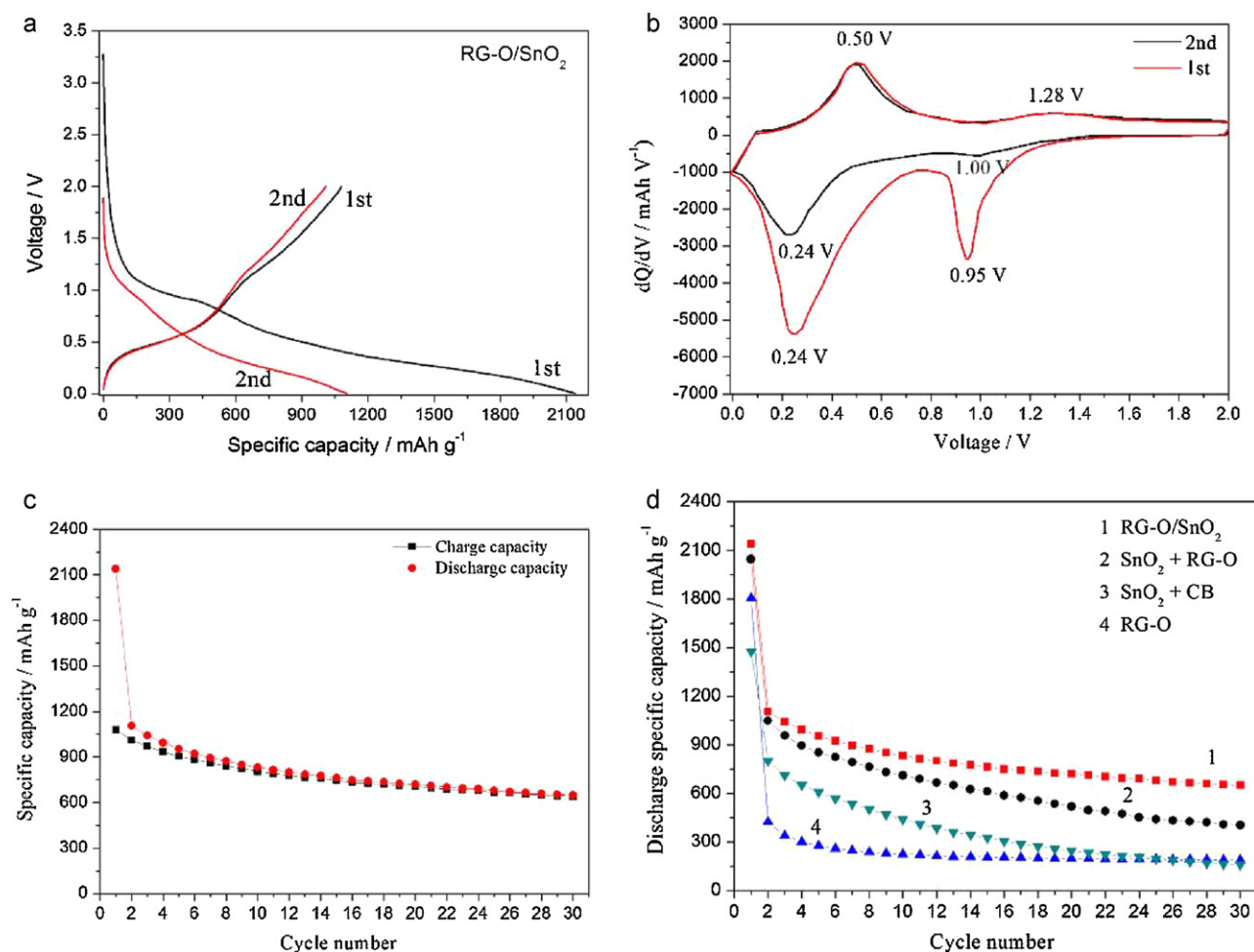


After the first discharge, the oxidation peak at  $0.50\text{ V}$  and  $1.28\text{ V}$  during charging, and the reduction peaks at  $1.00\text{ V}$  and  $0.24\text{ V}$  during the subsequent discharging, are related to the decomposition and formation of various  $\text{Li}_x\text{Sn}$  alloys as described in Eq. (5).

For the complete reduction of  $\text{SnO}_2 \rightarrow \text{Li}_x\text{Sn}$  ( $0 \leq x \leq 4.4$ ), one would expect a maximum uptake of  $8.4\text{Li}/\text{SnO}_2$  ( $\sim 1494\text{ mAh g}^{-1}$ ). For this reaction,  $4\text{Li}$  results from the formation of  $\text{Li}_2\text{O}$  (Eq. (4)), and  $4.4\text{Li}$  are due to the formation of  $\text{Li}_x\text{Sn}$  alloys (Eq. (5)). After the first cycle, it should have  $4.4\text{Li}$  theoretical capac-



**Fig. 1.** SEM images of (a and b) unannealed RG-O/ $\text{SnO}_2$ , and (c and d) RG-O/ $\text{SnO}_2$ .



**Fig. 2.** Electrochemical performance of the RG-O/SnO<sub>2</sub> composite. The specific capacities are based on the mass of SnO<sub>2</sub> in the composite. (a) Discharge/charge profiles of RG-O/SnO<sub>2</sub> for the first and second cycles at the current density of 50 mA g<sup>-1</sup>. (b) Derivative curves of the first and second cycles for RG-O/SnO<sub>2</sub>. (c) Cycling performance of RG-O/SnO<sub>2</sub> composite at a current density of 50 mA g<sup>-1</sup>. (d) Comparison of cycling performance of RG-O/SnO<sub>2</sub>, SnO<sub>2</sub> mixed physically with RG-O, SnO<sub>2</sub> mixed physically with carbon black (CB) in the same weight ratio as RG-O/SnO<sub>2</sub>, and RG-O.

ity ( $\sim 782 \text{ mAh g}^{-1}$ ). However, the  $2140 \text{ mAh g}^{-1}$  capacity on the first discharge is higher than  $1494 \text{ mAh g}^{-1}$ , and  $1080 \text{ mAh g}^{-1}$  capacity on the first charge is higher than  $782 \text{ mAh g}^{-1}$ . What gives rise to this ‘excess capacity’? The excess capacity appears to originate from electrolyte decomposition in the low-potential region, and thus perhaps the subsequent formation of an organic layer on the surface of the particles [23,24], as well as Li insertion/extraction (or simple decoration on open surfaces) of the RG-O platelets. The Li insertion/extraction/decoration on the surface of RG-O may play a major role in the overall electrochemical process and could be the primary reason for the excess capacity of the RG-O/SnO<sub>2</sub> composite electrode. By comparison, the first cycle of various other types of composites (see Fig. S5) shows that the first charge capacity of  $1080 \text{ mAh g}^{-1}$  for RG-O/SnO<sub>2</sub> is higher than that of 1020, 430 and  $767 \text{ mAh g}^{-1}$  for SnO<sub>2</sub> mixed physically with RG-O (indicated as SnO<sub>2</sub> + RG-O), for RG-O itself, and for SnO<sub>2</sub> mixed physically with carbon black (indicated as SnO<sub>2</sub> + CB), respectively. The results indicate that the RG-O/SnO<sub>2</sub> composite has more lithium insertion/extraction sites. This is perhaps because the SnO<sub>2</sub> nanoparticles are anchored on the surface of the RG-O platelets and thus can act as spacers between the RG-O platelets during discharging and charging, leading to higher discharge and charge capacities.

Fig. 2c shows the cycle performance of the RG-O/SnO<sub>2</sub> composite at  $50 \text{ mA g}^{-1}$  between 2.0 and 0.005 V. The discharge capacities

of the electrode in the first, 10th, 20th and 30th cycles are 2140, 834, 720 and  $649 \text{ mAh g}^{-1}$ , respectively, showing that the RG-O/SnO<sub>2</sub> composite has a much higher capacity than graphite. The coulombic efficiency of the first cycle is 50.5%. After 10 cycles, the coulombic efficiency is greater than 97%, which is higher than 91% of ‘SnO<sub>2</sub> + RG-O’, indicating that the composite has good capacity retention (see Fig. S6).

The high capacity and good cycling stability of the RG-O/SnO<sub>2</sub> composite as an anode material are attributed to the intimate contact between the SnO<sub>2</sub> nanoparticles and RG-O platelets. The uniform mixture and interaction between SnO<sub>2</sub> nanoparticles and RG-O platelets can accommodate the volume change of the nanoparticles during discharging and charging, and prevents the aggregation of the nanoparticles (see Fig. S7) as well as the restacking of RG-O platelets, which likely enhances cycle stability.

A comparison of the discharge cycling performance of RG-O/SnO<sub>2</sub>, SnO<sub>2</sub> + RG-O, RG-O, and SnO<sub>2</sub> + CB is shown in Fig. 2d. After 30 cycles, RG-O shows about 44.2% retention ( $187 \text{ mAh g}^{-1}$ ) of the second discharge capacity ( $423 \text{ mAh g}^{-1}$ ), whereas the SnO<sub>2</sub> + CB composite exhibits about 20.0% retention ( $160 \text{ mAh g}^{-1}$ ) of the second discharge capacity ( $801 \text{ mAh g}^{-1}$ ). It shows that the specific capacity of SnO<sub>2</sub> + CB fades faster than that of RG-O. On the other hand, RG-O/SnO<sub>2</sub> exhibits  $1105 \text{ mAh g}^{-1}$  for the second discharge capacity, higher than  $1048 \text{ mAh g}^{-1}$  of SnO<sub>2</sub> + RG-O. Furthermore, its cyclic performance is significantly enhanced as

seen from curve 1 in Fig. 2d. After 30 cycles, the discharge capacity was  $649 \text{ mAh g}^{-1}$ , while the specific capacity of  $\text{SnO}_2 + \text{RG-O}$  was  $404 \text{ mAh g}^{-1}$ .  $\text{SnO}_2 + \text{RG-O}$  decreased faster than  $\text{RG-O/SnO}_2$  during cycling. The comparison of the cyclic performance among  $\text{RG-O/SnO}_2$ ,  $\text{RG-O}$ ,  $\text{SnO}_2 + \text{RG-O}$  and  $\text{RG-O+CB}$  composites shows that the total specific capacity of the  $\text{RG-O/SnO}_2$  composite is higher than the sum of individual  $\text{SnO}_2$  and  $\text{RG-O}$  materials, or that of  $\text{SnO}_2 + \text{RG-O}$  in the same weight ratios, indicating a positive synergistic effect of  $\text{RG-O}$  platelets and  $\text{SnO}_2$  nanoparticles in the composite for enhanced electrochemical performance.

#### 4. Conclusions

In summary, a simple approach is used to fabricate a composite composed of  $\text{RG-O}$  platelets decorated with  $\text{SnO}_2$  nanoparticles for use as a Li-ion battery anode. This  $\text{RG-O/SnO}_2$  composite has a capacity of  $2140 \text{ mAh g}^{-1}$  and  $1080 \text{ mAh g}^{-1}$  for the first discharge and charge, respectively, at a current density of  $50 \text{ mA g}^{-1}$ , and good capacity retention with a capacity of  $649 \text{ mAh g}^{-1}$  after 30 cycles. Our synthesis method can be readily adapted to prepare other composites containing  $\text{RG-O}$  as a conducting additive that, in addition to supporting metal oxide nanoparticles, can also provide additional Li binding sites to further enhance capacity.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2011.04.015.

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