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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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⁻¹[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: with a high charge/discharge rate and a higher reversible capacity. Therefore, it is essential 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-SnO₂ composite by (i) homogeneous precipitation of SnCl₄ 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 SnO₂ nanoparticles, and finally (iii) annealing at 500 °C for 3 h under a nitrogen atmosphere with the aim of increasing crystallinity of the SnO₂ nanoparticles. As an anode material for Li-ion batteries, the RG-O/SnO₂ composite exhibited unprecedentedly high discharge and charge capacities of 2140 and 1080 mAh g⁻¹, respectively, for the first cycle, normalized to the mass of SnO₂ in the composite (~1712 and 864 mAh g⁻¹ respectively, based on the total mass of the composite), and good cycling performance with 649 mAh g⁻¹ 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 graphene oxide

Graphite oxide was synthesized from natural graphite by a modified Hummers method. Briefly, graphite powders (2 g; SP-1, Bay
Carbon, MI) and NaNO₃ (1 g; Aldrich, >99%) were mixed, then put into concentrated H₂SO₄ (96 ml; Fisher Scientific, 98%) in an ice bath. Under vigorous stirring, KMnO₄ (6 g; Fisher Scientific, 99.6%) was gradually added and the temperature of the mixture was kept below 20 °C. After removing the ice bath, the mixture was stirred at 35 °C in a water bath for 18 h. As the reaction progressed, the mixture became pasty with a brownish color. 150 ml H₂O was then slowly added to the pasty mixture. Addition of water into the concentrated H₂SO₄ 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 °C. After 240 ml H₂O, 5 ml of 30% H₂O₂ (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% 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–SnO₂ composite (RG-O/SnO₂)

The RG-O/SnO₂ composite was prepared by homogeneous precipitation with urea and subsequent reduction with hydrazine under microwave irradiation. In a typical experiment, 1 mmol SnCl₄·2H₂O (0.36 g; Fisher Scientific, 98%) and 2 mmol urea (1.20 g; Aldrich, 98%) were separately dissolved in 25 ml water. Then these solutions were slowly and sequentially added to 50 ml of graphite oxide suspension (2 mg ml⁻¹) and NaNO₃ (1 g; Aldrich, >99%) were mixed, then put into the microwave oven (Sensor Microwave Oven, DE68-00307A) and irradiated for an additional 60 s. When cooling to ambient temperature, 0.5 ml N₂H₄ (Aldrich, 98%) 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% 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.

#### 2.3. Characterization

The structure of the obtained RG-O/SnO₂ composite was characterized by X-ray diffraction (XRD) (X’pert, Philips) using CuKα 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 °C min⁻¹ under 20 ml min⁻¹ air flow. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos AXIS Ultra DLD XPS equipped with a 180° hemispherical energy analyzer to characterize the particles’ surface. Photoemission was stimulated by monochromated Al Kα 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 LiPF₆ 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/SnO₂ composite, SnCl₄ was hydrolyzed in the G-O suspension in the presence of urea under microwave irradiation. The molar ratio of SnCl₄ to urea was 1:2. This step yielded a uniform Sn(OH)₄ or SnO₂ 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 Sn(OH)₄, and subsequent decomposition of Sn(OH)₄ to SnO₂ as suggested by the following reactions:

\[
\text{CO(NH}_2\text{)}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + \text{CO}_2 + 2\text{OH}^- \tag{1}
\]

\[
\text{Sn}^{4+} + 4\text{OH}^- \rightarrow \text{Sn(OH)}_4^2- \tag{2}
\]

\[
\text{Sn(OH)}_4^2- \rightarrow \text{SnO}_2 + 2\text{H}_2\text{O} \tag{3}
\]

The Sn(OH)₄ and SnO₂ particles so produced likely anchor onto the surface of the G-O platelets through oxygen-containing functional groups, such as hydroxyl, epoxyl, 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 Sn(OH)₄ decomposes to SnO₂ nanoparticles as indicated in Eq. (3). The as-prepared composite obtained was characterized by XRD (see Fig. S1). The characteristic peaks of SnO₂ appear but are broad and weak, indicating the SnO₂ particles are amorphous and/or very small in size. In an attempt to improve the crystallinity of SnO₂ particles in the composite, the product was annealed at 500 °C for 3 h in a N₂ atmosphere. XRD of the annealed composite material shows that the diffraction peaks of crystalline SnO₂ nanoparticles are clearly distinguishable, and could be indexed to the tetragonal SnO₂ 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 3d₅/₂ and 3d₃/₂ spectrum is composed of single peak, respectively (see Fig. S2). And the Sn peak positions at ~487.03 eV for 3d₅/₂, and ~495.53 eV for 3d₃/₂ agree with the presence of SnO₂ [21]. The Raman spectrum has the characteristic peaks of the tetragonal phase of SnO₂ 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/SnO₂ and RG-O/SnO₂ composite was observed by scanning electron microscopy in Fig. 1. Fig. 1a and b shows that the as-prepared RG-O/SnO₂ composite consists of thin, crumpled RG-O platelets closely connected with each other to form a 3D network structure. It is too small for SnO₂ nanoparticles to be seen on the curved RG-O platelets. After annealing at 500 °C, the SnO₂ 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 SnO₂ 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/SnO₂ 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 SnO₂:RG-O:PTFE ratio of 76:19:5. Despite increasing the conductivity by adding those into
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/SnO$_2$ composite at a current density of 50 mAg$^{-1}$ in a voltage range of 2.0–0.005 V vs. Li$^+$/Li. The RG-O/SnO$_2$ composite delivers 2140 mAh g$^{-1}$ and 1080 mAh g$^{-1}$ capacities for the first discharge and charge, respectively, based on the mass of SnO$_2$ in the composite (The values are 1712 and 864 mAh g$^{-1}$, respectively, based on the total mass of the RG-O/SnO$_2$ composite). It can also be seen that the second discharge and charge capacities are 1105 and 1009 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/SnO$_2$ composite are presented in Fig. 2b. During the first discharge, the reduction peak at 0.95 V corresponds to the formation of a solid electrolyte interface (SEI) layer and Li$_2$O, and disappears after the first cycle. The reduction peak at 0.24 V corresponds to the formation of Li$_x$Sn alloys [21]:

$$4\text{Li}^+ + \text{SnO}_2 + 4\text{e}^- \rightarrow 2\text{Li}_2\text{O} + \text{Sn}$$ \hspace{1cm} (4)

$$x\text{Li}^+ + \text{Sn} + xe^- \rightleftharpoons \text{Li}_x\text{Sn} \hspace{1cm} (0 \leq x \leq 4.4)$$ \hspace{1cm} (5)

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

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

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

**Scheme 1.** Scheme for making RG-O/SnO$_2$ nanoparticle composite.
Fig. 2. Electrochemical performance of the RG-O/SnO₂ composite. The specific capacities are based on the mass of SnO₂ in the composite. (a) Discharge/charge profiles of RG-O/SnO₂ for the first and second cycles at the current density of 50 mA g⁻¹. (b) Derivative curves of the first and second cycles for RG-O/SnO₂. (c) Cycling performance of RG-O/SnO₂ composite at a current density of 50 mA g⁻¹. (d) Comparison of cycling performance of RG-O/SnO₂, SnO₂ mixed physically with RG-O, SnO₂ mixed physically with carbon black (CB) in the same weight ratio as RG-O/SnO₂, and RG-O.

ity (∼782 mAh g⁻¹). However, the 2140 mAh g⁻¹ capacity on the first discharge is higher than 1494 mAh g⁻¹, and 1080 mAh g⁻¹ capacity on the first charge is higher than 782 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/SnO₂ composite electrode. By comparison, the first cycle of various other types of composites (see Fig. S5) shows that the first charge capacity of 1080 mAh g⁻¹ for RG-O/SnO₂ is higher than that of 1020, 430 and 767 mAh g⁻¹ for SnO₂ mixed physically with RG-O (indicated as SnO₂ + RG-O), for RG-O itself, and for SnO₂ mixed physically with carbon black (indicated as SnO₂ + CB), respectively. The results indicate that the RG-O/SnO₂ composite has more lithium insertion/extraction sites. This is perhaps because the SnO₂ 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/SnO₂ composite at 50 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 mAh g⁻¹, respectively, showing that the RG-O/SnO₂ 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 “SnO₂ + RG-O”, indicating that the composite has good capacity retention (see Fig. S6).

The high capacity and good cycling stability of the RG-O/SnO₂ composite as an anode material are attributed to the intimate contact between the SnO₂ nanoparticles and RG-O platelets. The uniform mixture and interaction between SnO₂ 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/SnO₂, SnO₂ + RG-O, RG-O, and SnO₂ + CB is shown in Fig. 2d. After 30 cycles, RG-O shows about 44.2% retention (187 mAh g⁻¹) of the second discharge capacity (423 mAh g⁻¹), whereas the SnO₂ + CB composite exhibits about 20.0% retention (160 mAh g⁻¹) of the second discharge capacity (801 mAh g⁻¹). It shows that the specific capacity of SnO₂ + CB fades faster than that of RG-O. On the other hand, RG-O/SnO₂ Exhibits 1105 mAh g⁻¹ for the second discharge capacity, higher than 1048 mAh g⁻¹ of SnO₂ + 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 mAh g\(^{-1}\), while the specific capacity of SnO\(_2\) + RG-O was 404 mAh g\(^{-1}\). SnO\(_2\) + RG-O decreased faster than RG-O/SnO\(_2\) during cycling. The comparison of the cyclic performance among RG-O/SnO\(_2\), RG-O, SnO\(_2\) + RG-O and RG-O + CB composites shows that the total specific capacity of the RG-O/SnO\(_2\) composite is higher than the sum of individual SnO\(_2\) and RG-O materials, or that of SnO\(_2\) + RG-O in the same weight ratios, indicating a positive synergistic effect of RG-O platelets and 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 RG-O platelets decorated with SnO\(_2\) nanoparticles for use as a Li-ion battery anode. This RG-O/SnO\(_2\) composite has a capacity of 2140 mAh g\(^{-1}\) and 1080 mAh g\(^{-1}\) for the first discharge and charge, respectively, at a current density of 50 mA g\(^{-1}\), and good capacity retention with a capacity of 649 mAh g\(^{-1}\) after 30 cycles. Our synthesis method can be readily adapted to prepare other composites containing 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


References