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Abstract

Graphene with a single layer of carbon atoms densely packed in a honeycomb crystal lattice is one of attractive materials for the intercalation of lithium ion, but it has low volumetric capacity owing to low tap density. We report a method for in situ growth of SnO₂ on graphene nanosheets (SGN) as anode materials for rechargeable lithium batteries. The results indicated that the SnO₂ nanoparticles with size in the range of 5-10 nm and a polycrystalline structure are homogeneously supported on graphene nanosheets. The charge and discharge capacities of SGN attained to 1559.7 and 779.7 mAh/g in the first cycle at a current density of 300 mA/g. The specific discharge capacities remained at 620 mAh·g⁻¹ in the 200th cycle. The SGN exhibits a superior Listorage performance with good cycle life and high capacity.

Keywords

rechargeable, materials, anode, advanced, nanosheets, batteries, graphene, lithium, sno₂, growth, situ

Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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In Situ Growth of SnO₂ on Graphene Nanosheets as Advanced Anode Materials for Rechargeable Lithium Batteries

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Graphene with a single layer of carbon atoms densely packed in a honeycomb crystal lattice is one of attractive materials for the intercalation of lithium ion, but it has low volumetric capacity owing to low tap density. We report a method for in situ growth of SnO₂ on graphene nanosheets (SGN) as anode materials for rechargeable lithium batteries. The results indicated that the SnO₂ nanoparticles with size in the range of 5-10 nm and a polycrystalline structure are homogeneously supported on graphene nanosheets. The charge and discharge capacities of SGN attained to 1559.7 and 779.7 mAh/g in the first cycle at a current density of 300 mA/g. The specific discharge capacities remained at 620 mAh·g⁻¹ in the 200th cycle. The SGN exhibits a superior Li-storage performance with good cycle life and high capacity.

Introduction

Graphene has attracted tremendous attention from both fundamental and applied science communities since it was first reported in 2004 (1). This nanostructure holds great potential because of the unique electronic (2) and mechanical properties (3). In particular, these materials have superior electric conductivity, high surface areas, chemical tolerance and a broad electrochemical window that have been very advantageous in the application of solar cells (4), hydrogen storage (5), lithium ion batteries (6) or capacitors (7). However, two disadvantages are inherent in a graphene anode for the intercalation of lithium ion: low volumetric capacity owing to low tap density and a specific capacity that is limited by the theoretical maximum capacity of the graphite structure (372 mAh·g⁻¹). Increasing the capacity of a graphite structure anode materials by modifying with high capacity Li-storage compounds, such as those derived from Sn (8), SnNi (9) and Si (10) is a demonstrated route to improvement.

In particular, SnO₂ has been proposed as one of a family of alternative anode materials with a high Li-storage capacity, but the practical use of this material has been frustrated by rapid fading in the capacity upon cycling, due to the severe volume changes that occur during lithium insertion and extraction. Various nanostructures of SnO₂, such as nanoparticles (11), nano-architecture (12), nanotubes (13), nanodisks (14) and carbon nanotube coated SnO₂ nanowire (15) have been developed in order to improve the

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cycling performance. Recently, SnO₂/graphene nanoporous electrodes by surrounding SnO₂ nanoparticles with graphene nanosheets to improve the capacity attained with increased cycle number was reported (16), the first charge and discharge capacity of the SnO₂/GNS are 1890 and 810 mAh/g at a current density of 50 mA/g. Li et al (17) develop a new method to prepare the processable aqueous dispersions of graphene nanosheet, herein, based on previous works, we report a method for in situ growth of SnO₂ on graphene nanosheets (SGN), and the charge and discharge capacities of the as-prepared SGN have a much better performance at the fast charge–discharge rate.

Experimental

Graphite oxide (GO) was synthesized from natural graphite powder (Grade 230, Asbury Carbons) using the Hummers method (17). After being purified by several runs of centrifugation/washing, 50 mg GO was exfoliated into water (100 mL) by ultrasonication for one hour to form GO suspension. 100 mg SnCl₂ (98 %) was put into 10 mL of distilled water inside a glass flask and then added 0.3 mL of HCl (38%). The GO suspension was added into the above SnCl₂ solution and the pH value was adjusted to 10 using 1 M NH₃·H₂O solution. This mixture was ultrasonicated for 5 min and was reduced with hydrazine hydrate (85 %) under stirring at 80°C for 24h. The final product of SGN was rinsed with distilled water.

The morphology and structure of the prepared SGN anode material was characterized by SEM (Hitachi S-900), TEM (JEOL JEM-2100F), powder XRD (D/max-2200/PC, Rigaku, 40 kV, 20mA, Cu Ka radiation) and Raman (Jobin Yvon HR800 confocal Raman system, 632.8 nm diode laser excitation). The anode was prepared by mixing 75 wt% SGN active materials, 15 wt.-% acetylene black and 10 wt.-% polyvinylidene difluoride and incorporated into cells with lithium foil counter electrode, UP3025 separator, and 1 M LiPF₆/DMC+EC (1:1, v/v). Charge-discharge capacity and cycling performance of battery were measured using a battery test system (LAND CT2001A model, Wuhan Jinnuo).

Results and discussion

As shown in Fig. 1a, the SEM image of the SGN takes on corrugations and scrollings, revealing that the structural manipulation of the nanosheets is successfully achieved even after supporting SnO₂ nanoparticles. Fig. 1b and c show typical TEM images of SGN. The surface of the SGN is coated with SnO₂ nanoparticles with an average diameter of 5-10 nm. The high-resolution TEM exhibits two distinct images, lines, and spherical shapes. The former are due to SGN, whereas the latter could be attributed to SnO₂ nanoparticles. It is quite clear that loosely packed SnO₂ nanoparticles are homogeneously distributed on the GNS. The selected area electron diffraction (SAED) (Fig. 1d) also proves that the as-prepared SGN has a polycrystalline structure and the polycrystalline rings ascribed to the {110}, {101}, {211} and {310} diffraction planes of tetragonal rutile-like SnO₂.

Fig. 2a shows the XRD patterns of SGN. The maximal diffraction peaks of both specimen are consistent with the tetragonal SnO₂ lattice constants as $a = 4.738 \text{ \AA}$ and $c = 3.187 \text{ \AA}$ (JCPDS 41-1445), which is consistent with the result of TEM and confirms that the specimen are mainly constituted of SnO₂. No obvious peaks corresponding to SnCl₂, Sn or other tin oxides are observed. Raman spectroscopy is a powerful nondestructive tool used to characterize carbonaceous materials, particularly for distinguishing ordered and disordered crystal structures of carbon. The Raman spectrum

of the SGN (Fig. 2b) contains both G (corresponding to E_{2g} phonon of C sp² atoms) and D bands (a breathing mode of κ-point phonons of A_{1g} symmetry) at 1588.1 and 1324.7 cm⁻¹, respectively. The ratio of D to G band intensity of SGN is similar to the reduced GO (18), suggesting that a similar partially ordered graphite crystal structure is present.

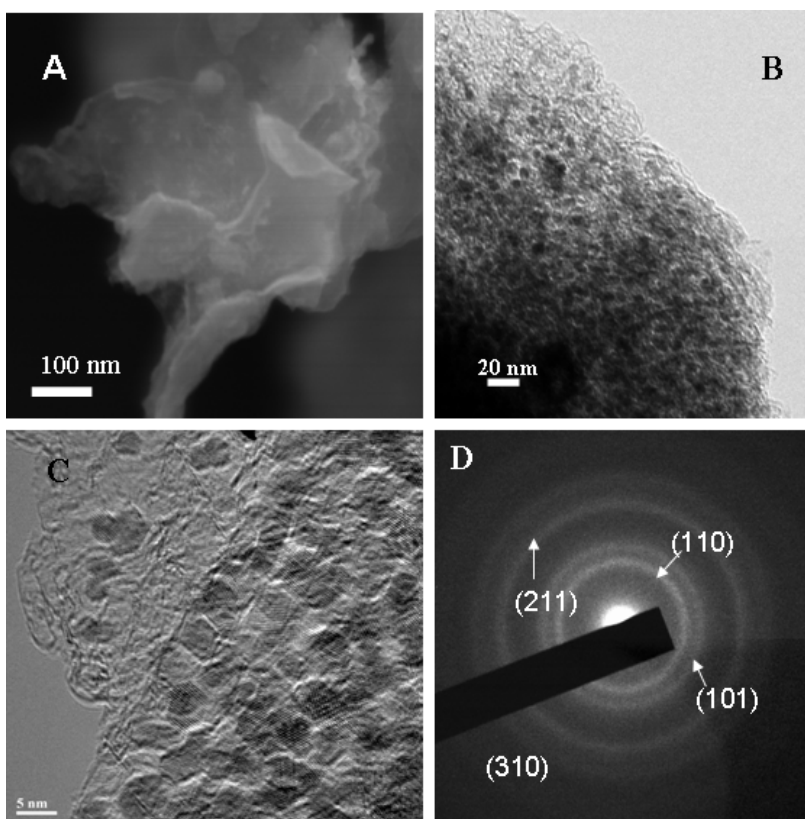


Fig. 1. SEM image (a), high-resolution TEM (b), (c) and selected area electron diffraction pattern (d) of SGN

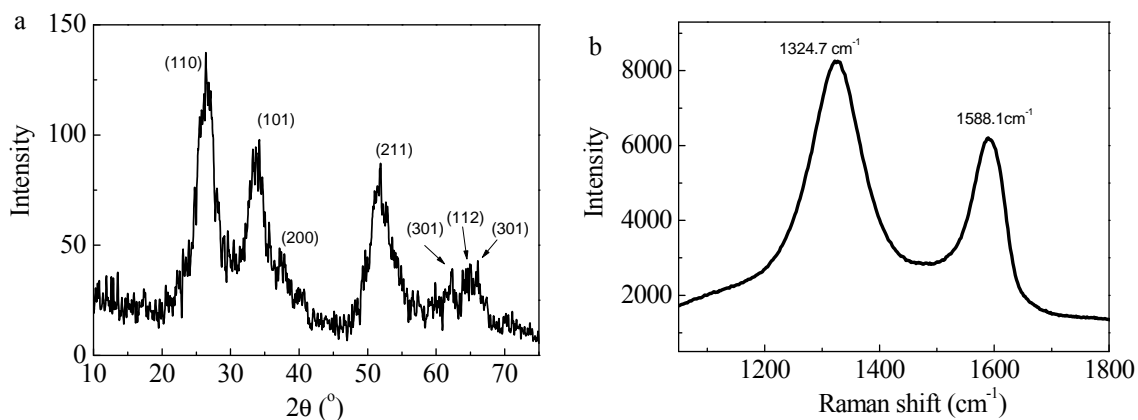
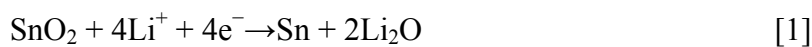
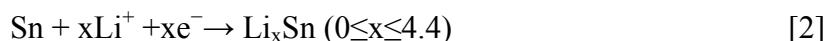


Fig. 2. XRD pattern (a) and Raman spectrum (b) of SGN

The SGN is evaluated as an anode material for the intercalation of lithium ion. In theory, SnO₂ has a higher reversible specific charge capacity than that of conventional graphite anodes because of the ability of Sn to alloy with lithium to a stoichiometry of Li_{4.4}Sn:





During the first charge and discharge process, SnO_2 will irreversibly reduced to form Sn metal when reacts with Li ion as described in Eq. 1 and the stored lithium ions will not be released, resulting in an irreversible capacity. Further charging (0.9-0.2 V) lead to formation of Li-Sn alloys. The reaction is reversible, and the lithium ions will be released when the Li_xSn decomposes (Eq. 2). As shown in Fig. 3a, the experimental values for the first cycle charge (Li^+ insertion) and discharge (Li^+ extraction) capacities are very high, at 1559.7 and 779.7 mAh/g, respectively, measured at a current density of 300 mA/g. The initial capacity loss (50.0 %) could be attributed primarily to SnO_2 reduction; however minor capacity losses could be due to the formation of the solid electrolyte interface (SEI). Since some functional groups remain unreduced by hydrazine on the surface of SGN (17), the Li^+ stored in these locations are more difficulty to extract, accounting for the large disparity between the charge and discharge capacities.

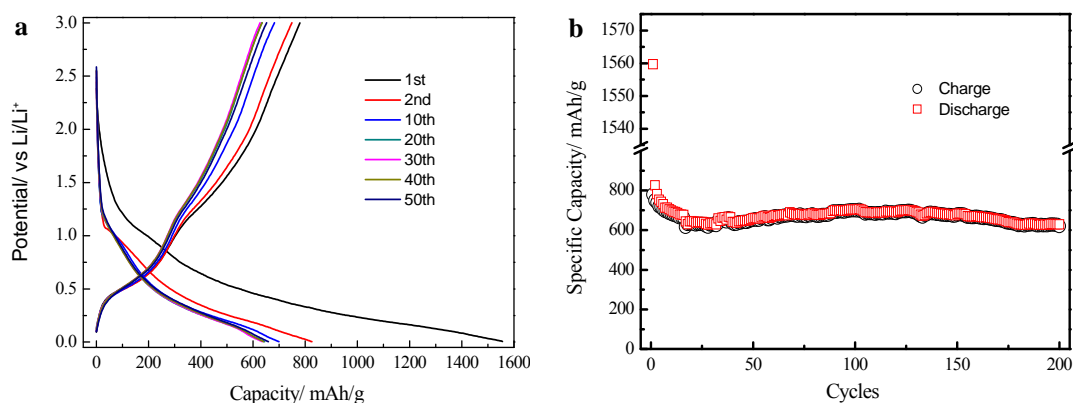


Fig. 3 Charge-discharge profiles (a) and cycling performance (b) of SGN anode material at a constant current density of 300 mA g^{-1} .

The change of reversible capacity of the as-prepared SGN at a constant charge-discharge current density of 300 mA/g is shown in Fig. 3b. It can be seen, the cycling performance over 200 cycles, the specific discharge capacities reaching 825.7, 699.4, 644.7, 636.0, 641.0 and 659.4 mAh/g at the second, 10th, 20th, 30th, 40th and 50th cycle, respectively, and remain at 620 mAh/g (>75% of the reversible capacity) in the 200th cycle. The voltage hysteresis of the as prepared SGN is similar to the carbonaceous anode material (9), it can be expound via the mechanism described in the literature (19). The as-prepared SGN anode shows high specific capacity and good cycling performance. It indicates that the mechanical integrity of the electrode is fully maintained. The reason can be interpreted as follows. Firstly, we know that the poor cyclability for SnO_2 as anodes is due to its large volume changes during the alloying and dealloying processes, which cause internal destructive changes in the electrode. In this work, Sn^{2+} ions are adsorbed on the surface of GO and then form a compact structure with GNS, similar to the structure with carbon nanotubes (20). This unique structure and excellent flexibility not only act as a buffer to relieve the strain associated with the volume variations, but also prevents the aggregation of SnO_2 nanoparticles upon cycling, which are believed to lessen the effects caused by volume change during cycling and thus alleviate the degrading of the electrode. Secondly, utilizing SGN not only advance the conductivity of the electrode, which would facilitate the electron transport and greatly decrease the Ohmic loss, but also offered a large surface area that made for enhancing the capacity (6,

7). Thirdly, in situ growth of SnO₂ nanoparticles on the surface of GNS resulted in marked abatement of the effective diffusion distance and increased the effective surface area. These act together to avoid the large capacity losses attributed to the alloying and dealloying processes.

Conclusions

In conclusion, we report a method for in situ growth of SnO₂ on GNS as an anode material for lithium ion batteries. The SnO₂ nanoparticles with size in the range of 5-10 nm are homogeneously supported on GNS. The as-prepared SGN anode exhibits a superior Li-storage performance with a good cycle life and high capacity. The first charge and discharge capacity of the SGN are 1559.7 and 779.7 mAh/g at higher charge-discharge rate (at a current density of 300 mA/g), which is much better than that of SnO₂ nanoparticles surrounded by GNS reported in literature (16). It indicates that the preparation process affects the structure and performance remarkably. The particular structure of the SGN can enhance the rate of electron transport and greatly decrease the Ohmic loss, and offer a large surface area that made for enhancing the capacity.

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