Carbon encapsulated ultrasmall SnO$_2$ nanoparticles anchoring on graphene/TiO$_2$ nanoscrolls for lithium storage

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**Abstract**

Amorphous carbon is coated on the surface of ultrasmall SnO$_2$ nanoparticles which are anchored on graphene/TiO$_2$ nanoscrolls via hydrothermal treatment, followed by annealing process. Transmission electron microscope images show that ultrasmall SnO$_2$ nanoparticles are anchored on graphene/TiO$_2$ nanoscrolls and further immobilized by the outermost amorphous carbon layer. The carbon encapsulated SnO$_2$@graphene/TiO$_2$ nanocomposites deliver high reversible capacities around 1131, 793, 621 and 476 mAh g$^{-1}$ at the current densities of 100, 250, 500, and 1000 mA g$^{-1}$, respectively. It is found that SnO$_2$ nanoparticles play a dominant role in the contributions of reversible capacity according to the cyclic voltammetry curves, voltage-capacity curves and dQ/dV vs. potential curves. The substrate of graphene/TiO$_2$ nanocomposites provides sufficient transport channels for lithium ions and high electron conductivity. While the outermost amorphous carbon layer prevents the peeling of SnO$_2$ nanoparticles from the substrate, therefore making them desirable alternative anode materials for lithium ion batteries.

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1. Introduction

Currently, lithium ion batteries (LIBs) have been considered as the most promising candidate for portable electronics and electrical/hybrid vehicles owing to their high energy density, long lifespan and environmental benignity.$^{[1,2]}$ TiO$_2$ has been widely studied as anode materials for LIBs due to their natural abundance, cost-effectiveness and excellent rate capability.$^{[3,4]}$ Furthermore, TiO$_2$ demonstrates quite small volume variation (3–4%) during lithium ions insertion/extraction,$^{[5]}$ leading to high structural stability and long cycle life. However, the drawbacks of poor electronic conductivity and low Li$^+$ diffusivity restrict its practical application for high-power LIBs.$^{[6]}$ A variety of approaches have been developed to surmount the tough issues, such as facet control,$^{[7]}$ surface coating$^{[8,9]}$ and nanorization$^{[10,11]}$. Graphene-based TiO$_2$ composite$^{[12–14]}$ have intrigued intensive interests of researchers, which are proved effective to improve the electronic conductivity and ion transport.

Tin dioxide (SnO$_2$) possesses high theoretical capacity but suffers from poor electrochemical performance$^{[15]}$ in terms of its dramatic volume expansion and shrinkage during alloying/dealloying ($>300$%),$^{[16]}$ which result in pulverization and severe destruction of the electrode.$^{[17]}$ Great efforts have been devoted to dealing with the conundrum. One of the most effective pathways is to fabricate yolk-shell SnO$_2$-based composites,$^{[18]}$ in which the voids can alleviate the volume change during lithiation and delithiation. Another approach is to synthesize hybrid nanostructures to immobilize SnO$_2$ with carbon-coating$^{[19,20]}$, which enhances the electronic conductivity, buffers the volume change and prevents the agglomeration of SnO$_2$ as well. Consequently, it is of great worth to combine high-capacity SnO$_2$ and structure-stable TiO$_2$ to design high-performance SnO$_2$@TiO$_2$ heterostructures which can tackle the pulverization and aggregation of SnO$_2$ nanocomposites.$^{[21–24]}$

In this paper, we report a facile strategy to synthesize carbon encapsulated SnO$_2$ nanoparticles anchoring on graphene/TiO$_2$ nanoscrolls via one-pot hydrothermal treatment and annealing process. The ultrasmall SnO$_2$ nanoparticles are anchored on the substrate of nanoscrolls and further immobilized by the outermost glucose-derived carbon layer, which prevent pulverization and peeling of SnO$_2$ nanoparticles from the substrate. The carbon
coated SnO$_2$@GNs/TiO$_2$ composites exhibit excellent cycling performance and high rate capability for high-power LIBs.

2. Experimental

2.1. Preparation of carbon capped SnO$_2$@graphene/TiO$_2$ and SnO$_2$@graphene composites

All the chemicals were used as received without further purification. Graphene oxide and anatase TiO$_2$ powder were mixed and transferred to a 100 mL autoclave, after hydrothermal treatment and ion-exchange, the resultant precursor was annealed to synthesize graphene/TiO$_2$ nanoscrolls (GNs/TiO$_2$) according to our previous report.[25] 0.5 g of GNs/TiO$_2$ nanoscrolls was dispersed in 70 mL of deionized water (DI) under ultrasonication for 3 h, then 0.31 g of SnCl$_4$·5H$_2$O was added and stirred for 1 h at ambient temperature. After 0.1 g of glucose was added to the above mixture and stirred for 6 h, the suspension was transferred to a 100 mL autoclave and hydrothermally treated at 200 °C for 24 h, followed by centrifugation and washing with DI. Then the resulted products were dried at 80 °C and annealed at 400 °C for 2 h in N$_2$ atmosphere to prepare carbon capped SnO$_2$@graphene/TiO$_2$ composites (SnO$_2$@GNs/TiO$_2$). SnO$_2$/graphene composites (SnO$_2$/GNs) were synthesized through the same synthesis process with SnCl$_4$·5H$_2$O and graphene oxide powder without carbon capsulation.

2.2. Materials Characterization

Field emission scanning electron microscopy (FESEM, ZEISS AURIGA FIB-SEM, Germany) and high-resolution transmission electron microscopy (HRTEM, LIBRA 200 FE, ZEISS, Germany) were performed to characterize the morphology and crystalline microstructure of the products. Nitrogen adsorption-desorption analysis was conducted on ASAP 2020 apparatus (Micromeritics Inc., USA). X-ray diffraction (XRD) patterns were recorded on DMAX-2500 PC X-ray spectrometer (Rigaku Corporation, Japan) with Cu Kα radiation (λ=1.5406Å). Fourier transform infrared (FTIR) spectrometry was carried out on Nicolet 5DXC (Thermo Nicolet, USA). Thermogravimetry (TG) curves were monitored on a thermal instrument (Netzsch STA 449 C, Germany).

2.3. Electrochemical Measurements

Electrochemical tests were performed using two-electrode CR2430 coin-type cells at ambient temperature. The working electrodes were prepared by mixing the active materials, carbon black, and poly vinylidene fluoride (PVDF) in a weight ratio of 70:15:15 in N-methyl-2-pyrrolidone (NMP) and pasting the mixture on a pure copper foil. A lithium foil was used as the counter electrode and a microporous polypropylene film (Celgard 2500) was used as the separator. The electrolyte used was 1 M LiPF$_6$ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v). The coin cells were assembled in a high-purity argon-filled glove box (Super 1220/750, Mikrouna, China). Cyclic voltammetry (CV) tests were implemented on an electrochemical workstation (Solartron 1287/1260 8w, USA). Galvanostatic charge/discharge tests were conducted on a battery test system (Arbin BT 2000, USA) in a voltage range of 0.01~3.00 V at different current densities.

3. Results and discussion

The synthesis process of carbon encapsulated SnO$_2$@GNs/TiO$_2$ nanoscrolls is schematically illustrated in Fig. 1. Graphene nanosheets and TiO$_2$ nanoparticles are hydrothermally treated, followed by ion-exchange and heat treatment to prepare GNs/TiO$_2$ nanoscrolls.[25] Sn$^{4+}$ ions are attached on the substrate of GNs/TiO$_2$ nanoscrolls during stirring, and then they are accordingly immered in an aqueous glucose solution. After hydrothermal treatment, SnO$_2$ nanoparticles are in-situ anchored and encapsulated by pre-carbonized glucose. Finally the amorphous carbon capped SnO$_2$@GNs/TiO$_2$ composites are synthesized after annealing. The morphology and structure of SnO$_2$/GNs and SnO$_2$@GNs/TiO$_2$ composites were characterized by FESEM and TEM. As shown in Fig. 2(a) and (b), the size of SnO$_2$ nanoparticles in SnO$_2$/GNs composites ranges from 150~350 nm. SnO$_2$ nanoparticles are attached on the graphene nanosheets or percolated in the voids of graphene nanosheets. TEM images in Fig. 2(c) and (d) show that the GNs/TiO$_2$ nanoscrolls still remain hollow tubular structure even after SnO$_2$ nanoparticles anchoring with a diameter of 50~160 nm and length of several micrometers. It is worth mentioning that the SnO$_2$ nanoparticles are ultrasmall (4~8 nm), which are readily immobilized by a glucose-derived carbon layer (average thickness of ca. 3 nm) at the edge of SnO$_2$@GNs/TiO$_2$ composites in Fig. 2(e) and (f). Fig. 2(f) shows the HRTEM image of the square part in Fig. 2(e), the lattice fringes with d-spacings of 0.3397 and 0.3297 nm are ascribed to the (110) and (200) lattice planes of rutile-type SnO$_2$, respectively. The d-spacings of 0.3259 and 0.3267 nm are ascribed to the (110) lattice plane of rutile-type TiO$_2$ while the d-spacing of 0.2520 nm corresponds to the (101) lattice plane of TiO$_2$.

The crystallographic structure of SnO$_2$@GNs/TiO$_2$ and SnO$_2$/GNs composites were investigated by XRD. As shown in Fig. 3(a), the main diffraction peaks at ~ 27.3°, 35.8°, 40.9°, 54.0°, 56.3° and 68.7° in the SnO$_2$@GNs/TiO$_2$ composites can be well indexed to rutile-type TiO$_2$ (JCPDS card no.21-1276).[26] The primary TiO$_2$ (B) phase transformed to rutile-type TiO$_2$ during hydrothermal treatment as shown in Fig. 3(a), considering the high thermal stability of TiO$_2$ whose major phase transformation to rutile occurs above 700 °C in air.[27] While the small “bumps” emerged at 2θ = 38.9° and 61.9° are assigned to SnO$_2$ phase in SnO$_2$@GNs/TiO$_2$. The diffraction peaks of SnO$_2$/GNs composites are well coincided with JCPDS card no.41-1445.[21] Notably, both the diffraction peaks around 2θ = 26° in SnO$_2$@GNs/TiO$_2$ and SnO$_2$/GNs composites are quite strong, which are probably associated with the diffraction of graphene.

Nitrogen adsorption-desorption isothermal curves of the SnO$_2$@GNs/TiO$_2$ and SnO$_2$@GNs composites are displayed in Fig. 3(b). The SnO$_2$@GNs/TiO$_2$ present a typical type III curve with a H1 hysteresis loop,[21] indicating the presence of open-ended cylindrical pores in the composites, which are ascribed to the
nanoscrolled substrate of GNs/TiO₂. While the SnO₂/GNs composites exhibit a typical type III curve with a H₂ hysteresis loop, revealing abundant narrow pores between parallel plates of the graphene nanosheets in the SnO₂/GNs composites. The Brunauer-Emmett-Teller (BET) specific surface area and average pore volume of SnO₂@GNs/TiO₂ are 200 m² g⁻¹ and 0.62 cm³ g⁻¹, respectively, much higher than those of SnO₂/GNs composites (153 m² g⁻¹ and 0.41 cm³ g⁻¹, respectively). The monomodal pore size distribution of SnO₂@GNs/TiO₂ calculated by the Barrett-Joiner-Halenda (BJH) model is between 5–15 nm, which is obviously larger than the bimodal pore size distribution of SnO₂/GNs composites centered at 3–4 nm and 6–10 nm. The abundant pores in the SnO₂@GNs/TiO₂ provide sufficient accesses for the penetration and diffusion of lithium ions in the active materials.[28]

FTIR spectra of the as-prepared products were examined to distinguish the different chemical bonds in the composites. As shown in Fig. 3(c), the absorption peak at ~3440 cm⁻¹ associates with the stretching vibrations of hydroxyls of the –COOH groups, while the band at ~1630 cm⁻¹ corresponds to the O–H bending vibrations of water molecules.[29] The band at ~1115 cm⁻¹ relates to the C–C bonds of graphene and pyrolyzed carbon. The absorption peaks emerged at ~668 cm⁻¹ and ~542 cm⁻¹ in SnO₂@GNs/TiO₂ correspond to the stretching vibration modes of Ti–O–Ti bonds.[12] While the broad adsorption peaks at ~457 cm⁻¹ and ~620 cm⁻¹ are associated with the stretching vibration modes of O–Sn–O and Sn–O bonds,[21] respectively, confirming the existence of SnO₂ in SnO₂@GNs/TiO₂ composites.

Fig. 3(d) shows the TG curves of SnO₂@GNs/TiO₂ and SnO₂/GNs composites. The slight weight loss of 0.98wt% below 300°C is
ascribed to the removal of surface-adsorbed water owing to the large specific surface area of SnO2@GNs/TiO2 composites. The weight loss of 13.5wt% between 300~800 °C can be attributed to the combustion of carbon, including graphene and amorphous carbon in SnO2@GNs/TiO2 composites.[29] The weight loss of ~0.73wt% below 300°C in the SnO2@GNs composites is due to the removal of absorbing water, while about 1.04wt% of weight loss between 300~400 °C is associated with the decomposition of oxygen-containing functional groups in graphene oxides.[30] It can be calculated that the weight loss between 400~800 °C is 17.4wt%, owing to the combustion of graphene nanosheets, which is close to the initial addition of graphene nanosheets (20 wt%) in the synthesis process.

To understand the electrochemical behavior during lithiation and delithiation in SnO2@GNs/TiO2 composites, CV measurements were carried out at a scan rate of 0.02 mV s⁻¹ in the voltage range of 0.0~3.0 V. As presented in Fig. 4 (a), two well-defined cathodic peaks at ~1.07 V and ~0.16 V can be observed in the first cycle of SnO2@GNs composites. The peak at ~1.07 V corresponds to the conversion of SnO2 to Sn and Li2O upon lithiation (as shown in equation (1)), resulting in the formation of solid electrolyte interface (SEI). [31] While the peak appeared at ~0.16 V can be ascribed to the formation of alloy phases of Li₅Sn (equation (2)). [17,32] The small bumps at ~0.03 V are assigned to the subsequent lithium insertion into the graphene nanosheets. [33] In the anodic process, there are three oxidation peaks presented at ~0.5, 1.2, 1.8 V, respectively, associating with the extraction of lithium ions from Li₅Sn alloys, which are in accordance with previous reports. [20,28] It is known that the insertion/extraction of lithium ions in TiO2 mainly occurs in the voltage range of 1.5~2.1 V.[13] In the case of SnO2@GNs/TiO2 composites, the anodic peaks ranging from 1.5~2.0 V are obviously broadened, which are related to the delithiation in the rutile-type TiO2 by equation (3), as shown in Fig. 4 (b). [26] The anodic peaks are too broad to appear, demonstrating that the rutile-type TiO2 (theoretical specific capacity: 170 mAh g⁻¹) contributes much less capacity comparing with SnO2 in the SnO2@GNs/TiO2 composites.

SnO2 + 4Li⁺ + 4e⁻ → 2Li2O + Sn (1)
Sn + xLi⁺ + xe⁻ → LiₓSn (0 ≤ x ≤ 4.4) (2)
TiO2 + yLi⁺ + ye⁻ → LiₓTiO2 (0 ≤ y ≤ 0.5) (3)

The electrochemical performances of SnO2@GNs/TiO2 and SnO2@GNs were evaluated by galvanostatic charge/discharge cycling within a cut-off window of 0.01~3.00 V. As shown in Fig. 5 (a), the typical voltage vs. capacity curves at different current densities indicate that SnO2@GNs/TiO2 deliver an initial discharge capacity of 2470 mAh g⁻¹ and a charge capacity of 1131 mAh g⁻¹ at the current density of 100 mA g⁻¹ with a coulombic efficiency of 45.7%. Based on our work and previous reports,[19,34] it can be
deduced that the reaction of equation (1) would be reversible to some extent. According to the redox conversion of SnO$_2$ (equation (1)) and alloying mechanism of Li$_x$Sn (equation (2)), the maximum theoretical capacity of SnO$_2$ is calculated to be 1493 mAh g$^{-1}$,[34] which is higher than our results (1131 mAh g$^{-1}$). The carbon encapsulated SnO$_2$@GNs/TiO$_2$ composites possess high specific surface area (200 m$^2$ g$^{-1}$), ultrasmall SnO$_2$ nanoparticles (4–8 nm) and abundant mesopores (5–15 nm), which can be beneficial to such a high reversible capacity. The large irreversible capacity loss of SnO$_2$@GNs/TiO$_2$ in the first cycle can be attributed to the formation of SEI, which consumes a large number of solvent lithium ions.[32] Notably, a voltage plateau appears at ~1.05 V in the discharge process, correspondingly, a voltage plateau at ~0.5 V as well as a slope in the voltage range of 1.0–1.7 V can be seen in the charge process. However, with the current densities increase, the voltage plateau at ~0.5 V gradually disappears and the slope between 1.0–1.7 V becomes quite steep, indicating that major capacity increases in the voltage range of 0.5–1.0 V. It can be deduced that SnO$_2$ nanoparticles play a dominant role in lithium storage in SnO$_2$@GNs/TiO$_2$ at high current densities.[19] The voltage charge/discharge profiles of SnO$_2$@GNs/TiO$_2$ are illustrated in Fig. 5(b). With the cycle number increases, the charge voltage plateaus in the range of 0.3–0.7 V become shortened and declining slopes gradually appear, indicating unavoidable capacity decay. Fig. 5(c) and (d) show the dQ/dV vs. potential curves which are quite similar to the CV curves in Fig. 4(b). The peaks at ~0.5 V associated with the dealloying of SnO$_2$ can be clearly seen as the current density increases and the cycles continue. The large areas between 0.3–1.5 V (primary voltage range of alloying/dealloying in SnO$_2$) show the major capacity increase, further confirming the dominant lithium-storage role of SnO$_2$ in SnO$_2$@GNs/TiO$_2$ composites.

The rate performances of SnO$_2$@GNs/TiO$_2$ and SnO$_2$/GNs at various current densities in the range of 100–1000 mAh g$^{-1}$ (Fig. 5(e)). SnO$_2$@GNs/TiO$_2$ exhibit reversible capacities around 1131, 793, 621 and 476 mAh g$^{-1}$ at the current densities of 100, 250, 500, and 1000 mAh g$^{-1}$, respectively, which are much higher than those of SnO$_2$/GNs (1056, 713, 588, 394 mAh g$^{-1}$). Considering the lower content of SnO$_2$ in the SnO$_2$@GNs/TiO$_2$ composites (~3.85wt % of GNS, ~9.65wt% of amorphous carbon, ~19.02wt% of SnO$_2$, ~67.48wt% of TiO$_2$ calculated according to the raw reagents), the SnO$_2$@GNs/TiO$_2$ composites exhibit much better rate capability than the SnO$_2$/GNs composites. The specific capacities of both SnO$_2$@GNs/TiO$_2$ and SnO$_2$/GNs composites decrease obviously at the current density of 100 mAh g$^{-1}$, but the cycle stability is obviously enhanced as the current densities increase. The reversible capacity of the SnO$_2$@GNs/TiO$_2$ composites recovers to 638 mAh g$^{-1}$ when the current density returns to 100 mAh g$^{-1}$. To investigate the cycling performances of SnO$_2$@GNs/TiO$_2$ and SnO$_2$/GNs, the coin cells were tested at 500 mAh g$^{-1}$ for 200 cycles after aging at 100 mAh g$^{-1}$ for 5 cycles (Fig. 5(f)). SnO$_2$@GNs/TiO$_2$ deliver a charge capacity of 884 mAh g$^{-1}$ with a coulombic efficiency of 98.5%. The irreversible capacity loss (10%) is irreversible owing to the trapping of lithium ions during insertion/extraction in the solid state.[35] The specific capacity of SnO$_2$@GNs/TiO$_2$ tends to fade in the first 50 cycles and becomes stable during the following 50 cycles. Notably, the specific capacity of SnO$_2$@GNs/TiO$_2$ increases gradually, reaching a reversible capacity of 524 mAh g$^{-1}$ over 200 cycles. However, the specific capacity of the SnO$_2$/GNs composites fluctuates after the first 50 cycles, delivering a reversible capacity of 304 mAh g$^{-1}$.

For comparison, recent reports about SnO$_2$@ TiO$_2$ (and graphene) composites are listed in Table 1. SnO$_2$@GNs/TiO$_2$ in our work deliver higher reversible capacity and/or longer cycle life than those related work at the similar current density. The excellent electrochemical performance can be ascribed to the synergetic effects between GNS/TiO$_2$ substrates, SnO$_2$ nanoparticles and the outermost carbon layer.[21,23,36] The hollow tubular graphene/TiO$_2$ nanoscrolls can serve as an effective buffer to alleviate the remarkable volume expansion and shrinkage of SnO$_2$ nanoparticles during alloying/dealloying. Furthermore, the outermost glucose-derived carbon layer dramatically immobilizes the ultrasmall SnO$_2$ nanoparticles, thus prevents their peeling from the substrate of GNS/TiO$_2$ nanoscrolls, as SnO$_2$ nanoparticles contribute predominant capacity in SnO$_2$@GNs/TiO$_2$. So the high electrochemical performance of SnO$_2$@GNs/TiO$_2$ can be attributed to both the high reversible capacity of SnO$_2$, structural stability of TiO$_2$ nanoscrolls and high electronic conductivity of graphene. Based on our research and previous reports, the reasons for the capacity increase along with cycling can be explained as below: (1) considering the capacity contribution from SnO$_2$ plays a dominant role in the SnO$_2$@ graphene/TiO$_2$ hybrid, the pseudocapacitive behavior of SnO$_2$ may lead to the increased capacity along with cycles. In the process of Li$^+$ insertion and de-insertion, inevitable pulverization of SnO$_2$ nanoparticles upon cycling generates more fresh cracks and micropores, which enlarge contact area with electrolytes, resulting in continuous formation of an organic polymer/gel like film. Sun et al. suggested that the reversible formation and decomposition of the organic polymer/gel like film provide extra interfacial lithium storage sites. [17,18] Recently Dunn et al. demonstrated that pseudocapacitive behavior occurs when lithium ions insert into mesoporous and nanocrystalline films.[37] (2) Wang and Shi et al. claimed that the conversion between SnO2 and Li$^+$ (equation (1)) could become reversible to some extent upon cycling, though it is initially considered irreversible.[34,38]
Fig. 5. (a) Charge/discharge voltage curves of SnO$_2$@GNs/TiO$_2$ composites at different current densities, (b) rate performances of SnO$_2$@GNs/TiO$_2$ and SnO$_2$/GNs composites, (c) and (d) $dQ/dV$ vs. potential curves of SnO$_2$@GNs/TiO$_2$, (e) charge/discharge voltage curves of SnO$_2$@GNs/TiO$_2$ composites in different cycles, (f) cycling performances of SnO$_2$@GNs/TiO$_2$ and SnO$_2$/GNs at the current density of 500 mA g$^{-1}$ between 0.01–3.00 V.

Table 1
List of recent work on SnO$_2$@TiO$_2$ (and graphene) composites as anode materials for lithium-ion battery.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Current density (mA g$^{-1}$)</th>
<th>Cycle number (N)</th>
<th>Reversible capacity after N cycles (mAh g$^{-1}$)</th>
<th>Publication year [Ref.]</th>
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<tr>
<td>TiO$_2$-supported-SnO$_2$ nanocomposites</td>
<td>156.4</td>
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<td>312</td>
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<tr>
<td>SnO$_2$ nanoparticles in hollow TiO$_2$ nanofibers</td>
<td>136.4</td>
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<td>~500</td>
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<tr>
<td>SnO$_2$@TiO$_2$ double-shell nanotubes</td>
<td>800</td>
<td>50</td>
<td>300</td>
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</tr>
<tr>
<td>Graphene-TiO$_2$-SnO$_2$ ternary nanocomposites</td>
<td>50</td>
<td>50</td>
<td>537</td>
<td>2013[41]</td>
</tr>
<tr>
<td>TiO$_2$/SnO$_2$/carbon hybrid nanofibers</td>
<td>30</td>
<td>100</td>
<td>442.8</td>
<td>2013[23]</td>
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<tr>
<td>SnO$_2$/TiO$_2$ core-shell composites</td>
<td>1000</td>
<td>30</td>
<td>505</td>
<td>2013[42]</td>
</tr>
<tr>
<td>TiO$_2$@SnO$_2$/graphene</td>
<td>160</td>
<td>30</td>
<td>600</td>
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<td>SnO$_2$@TiO$_2$/carbon cloth</td>
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<td>100</td>
<td>700</td>
<td>2014[43]</td>
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<tr>
<td>SnO$_2$ nanoparticles in hollow TiO$_2$ nanowires</td>
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<td>500</td>
<td>445</td>
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</tr>
<tr>
<td>SnO$_2$@graphene/TiO$_2$</td>
<td>500</td>
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4. Conclusions

In summary, we have designed a facile method to fabricate amorphous carbon encapsulated SnO$_2@$graphene/TiO$_2$. The SnO$_2@$graphene/TiO$_2$ exhibit a reversible capacity of 476 mAh g$^{-1}$ at the current density of 1000 mA g$^{-1}$. After 200 cycles at the current density of 500 mA g$^{-1}$, the reversible capacity of the composites remains 524 mAh g$^{-1}$. The high electrochemical performance of the composites can be attributed to the synergetic effects between the graphene/TiO$_2$ nanoscrolls, SnO$_2$ nanoparticles and amorphous carbon layer. Firstly, the hollow graphene/TiO$_2$ nanoscrolls effectively alleviate the remarkable volume expansion and shrinkage of SnO$_2$ nanoparticles, as well as provide sufficient channels for the fast transport of both electrons and lithium ions. Secondly, the outermost amorphous carbon layer dramatically immobilizes the ultrasmall SnO$_2$ nanoparticles and further enhances the electronic conductivity. This synthetic strategy will be promising in the fields of multi-component composites for energy storage and conversion.

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