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SnO_2 nano-spheres/graphene hybrid for high-performance lithium ion battery anodes

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Abstract

SnO_2 nano-spheres/graphene composite was fabricated via a simple one-step hydrothermal method with graphene oxide and $SnCl_4 \cdot 5H_2O$ as the precursors. The composite was characterized by X-ray diffraction, field-emission scanning electron microscopy, transmission electron microscopy and surface area measurement. It is shown that fine SnO_2 nano-spheres with an average size of 50–100 nm could be homogeneously deposited on graphene nano-sheets layer by layer. The structural feature enabled SnO_2 nano-spheres/graphene hybird as an excellent anode material in lithium ion battery. The composite possesses 1306 mA h g^{-1} of initial discharge capacity and good capacity retention of 594 mA h g^{-1} up to the 50th cycle at a current density of 100 mA g^{-1}. These results indicate that the composite is a promising anode material in high-performance lithium ion batteries.

Keywords: SnO_2 nanospheres; Graphene; Hybird; Lithium ion battery

1. Introduction

Since Sony introduced the first commercial lithium ion battery in 1991 [1], graphite, which has a theoretical capacity of 372 mA h g^{-1}, has been the primary material for anode [2]. However, the growing demand for high performance lithium rechargeable batteries promotes a search for new anode materials. Great efforts have been made to develop new anode materials with high capacity [3–5]. Recently, graphene, as a kind of new carbon material, has aroused special attention due to its two-dimensional nanostructure since it was first reported in 2004 [6]. This unique nano-structure holds great potential because of its excellent electronic conductivity, mechanical properties and high surface area (2600 m^2/g) [7]. However, graphene sheets always naturally stack into multilayers and therefore lose their high surface area and intrinsic chemical and physical properties.

For anode materials, various metal oxides have been extensively investigated in order to replace the commonly used graphite [8–10]. Among them, tin oxide (SnO_2) stands out, due to its superior capacities(theoretical capacity 790 mAh g^{-1}) [11] as compared to graphite. It is known that the practical application of SnO_2 as anode is hampered due to its poor cyclability, resulting in the severe volume expansion and contraction during the alloying–dealloying cycles with Li^+ [12]. To improve the electrochemical capacity and cyclicality, various nano-structures of SnO_2, such as nano-particles [13], nano-rods [14], nano-wires [15], nano-tubes [12], nano-boxes [16], hollow spheres [17], and mesoporous structures [18], were prepared and studied. These nanomaterials, however, either suffer from high synthesis cost or aggregations among them that leads to low capacity and large volume change. It has been suggested that carbon-coating is an effective way to improve the cycling performance of non-carbonaceous anode materials, and good preliminary evidence has also been demonstrated [19,20]. Graphene, due to excellent electronic conductivity and high surface area, can act as a buffer layer that cushions the stress induced by volume expansion or contraction, increasing the electronic conductivity of the nano-composite electrode[21,22]. Thus, in this paper, a hybrid SnO_2/graphene nano-composite was synthesized via a facile and efficient hydrothermal method to get a material of lithium ion battery anodes with high capacity and stable performance.

2. Experimental details

2.1. Synthesis of samples

Graphite powder (50 mesh, with purity $>99.99\%$) was obtained from Alfa Aesar. All other chemicals (purchased from

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Aldrich etc.) used in this experiment were of analytical grade and were used without further purification.

Graphene oxide was synthesized from natural flake graphite powder by a modified Hummers method [23]. 0.1 g of graphene oxide was dispersed in 20 mL of deionized water and 20 mL of ethanol. Subsequently, 0.2 g of $SnCl_4 \cdot 5\,H_2O$, 0.24 g of NaOH and 0.42 g of Hexadecyl trimethyl ammonium bromide (CTAB) were added into the above suspension. After stirring for 20 min at room temperature, the mixture was transferred into a PTFE (polytetrafluoroethylene)-lined autoclave of 50 ml capacity, heated at 200 °C for 12 h, and then cooled down to room temperature naturally. The as-synthesized products were isolated by centrifugation, washed several times with deionized water and absolute ethanol and finally dried in air at 70 °C for 24 h. The bare SnO_2 was prepared by same method, except that the amounts of graphene oxide were 0.1 g.

2.2. *Samples characterization*

The samples were analyzed by X-ray diffraction (D/max 2550 V, Cu/Ka radiation, $\lambda = 1.5406$ Å, $2\theta = 10$–80°, Germany), field emission scanning electron microscopy (FEI NOVA 400, USA), transmission electron microscope (LIBRA 200FE, Germany) and an automatic specific surface area measuring equipment (ASAP 2020M, USA).

2.3. *Electrochemical measurements*

Coin cells were made to test the electrochemical performance with a Li foil as the counter electrode. The working electrode was prepared by mixing SnO_2 nano-spheres/graphene as active materials whereas 80 wt% carbon black, 10 wt% and polyvinylidone difluoride (PVDF) and 10 wt% in N-methyl-2-pyrrolidone (NMP) to form a homogeneous slurry. 1 M solution of $LiPF_6$ in a 50:50 v/v mixture of ethylene carbonate (EMC) and diethyl carbonate (DEC) for the electrolyte. The coated electrodes were dried in a vacuum oven at 120 °C for 12 h. Electrochemical measurements were carried out using discharge of galvanostatic charge in the voltage range 0–3.0 V vs. Li/Li^+ at the current densities of 100 mA g^{-1} via a battery testing system (Ningbo Baite Testing Equipment Co., China). Cyclic voltammetry (CV) curves were collected at 0.2 mV s^{-1} in the range of 0–3.0 V.

3. Results and discussion

The XRD pattern obtained from SnO_2 nano-spheres/graphene hybrids is shown in Fig. 1, together with those of the as prepared graphite oxide (GO) and bare SnO_2. The diffraction patterns of the hybrids (Fig. 1(c)) agree well with those of the cassiterite tetragonal crystalline phase of SnO_2 (JCPDS 41-1445[5]), indicating the strong crystalline nature of the SnO_2 nano-particles(Fig. 1(b)). The pure GO displays a strong (002) diffraction peak and a weak (100) diffraction peak (Fig. 1(a)). It is noted that there is no obvious (002) diffraction peak in the composites, due to the overlap of the diffraction peak for graphene oxide (002) facet with that of (110) facet for SnO_2.

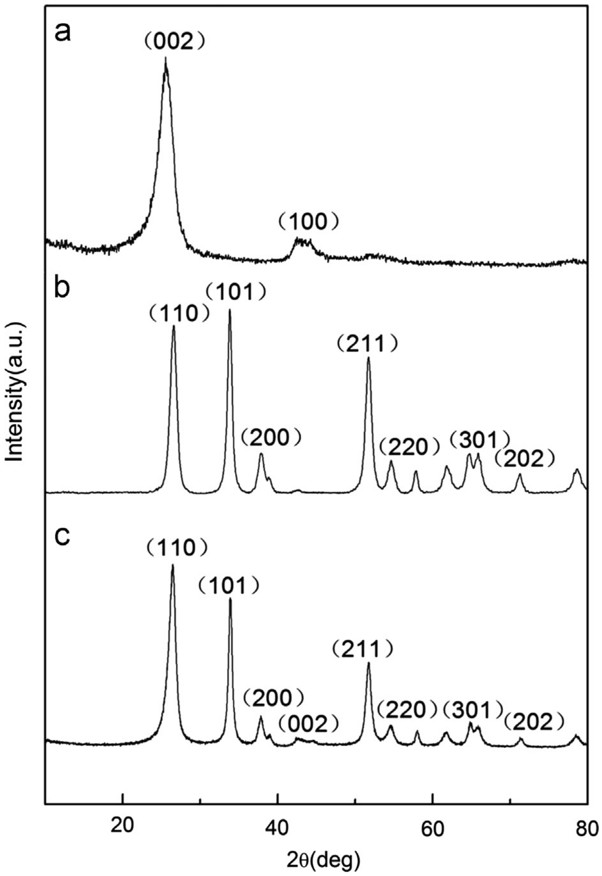

Fig. 1. XRD patterns of (a) graphene oxide, (b) bare SnO_2 and (c) SnO_2 nano-spheres/graphene composite.

To investigate the morphology of the materials, field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were performed on the SnO_2 nano-spheres/graphene hybrids. Fig. 2(c) and (d) presents a FESEM image of the composite material. Comparing with the bare SnO_2 and pure graphene oxide (Fig. 2(a) and (b)), it can be seen clearly that the SnO_2 nano-spheres are uniformly distributed on or in between the graphene nanosheets to form a layer by layer structure, by which graphene nano-sheet re-stacking and SnO_2 nano-spheres aggregation can be prevented. The TEM images of SnO_2/graphene (Fig. 2(e)) clearly illustrate that SnO_2 nano-spheres are distributed sporadically on the surface of graphene nano-sheets and that the diameters of the SnO_2 nano-sphere are about 50–100 nm, which is much smaller than that of pure SnO_2, indicating that graphene effectively prevents the SnO_2 nano-particle growth. The lattice fringes in the HRTEM image (Fig. 2(f)) further confirm the single crystal nature of the SnO_2 nano-particles; meanwhile the interplanar distances of 0.336 and 0.261 nm can be identified as $d(110)$ and $d(200)$ of rutile SnO_2, respectively.

Fig. 3(a) shows the adsorption/desorption isotherm and pore size distribution curve of the SnO_2 nano-spheres/graphene composites. According to the Brunauer–Emmett–Telle (BET) method [24], the composite exhibits very high specific surface area of 81.5 m^2/g, which is much larger than that of the bare SnO_2 (9.67 m^2/g). Moreover, it shows an average pore

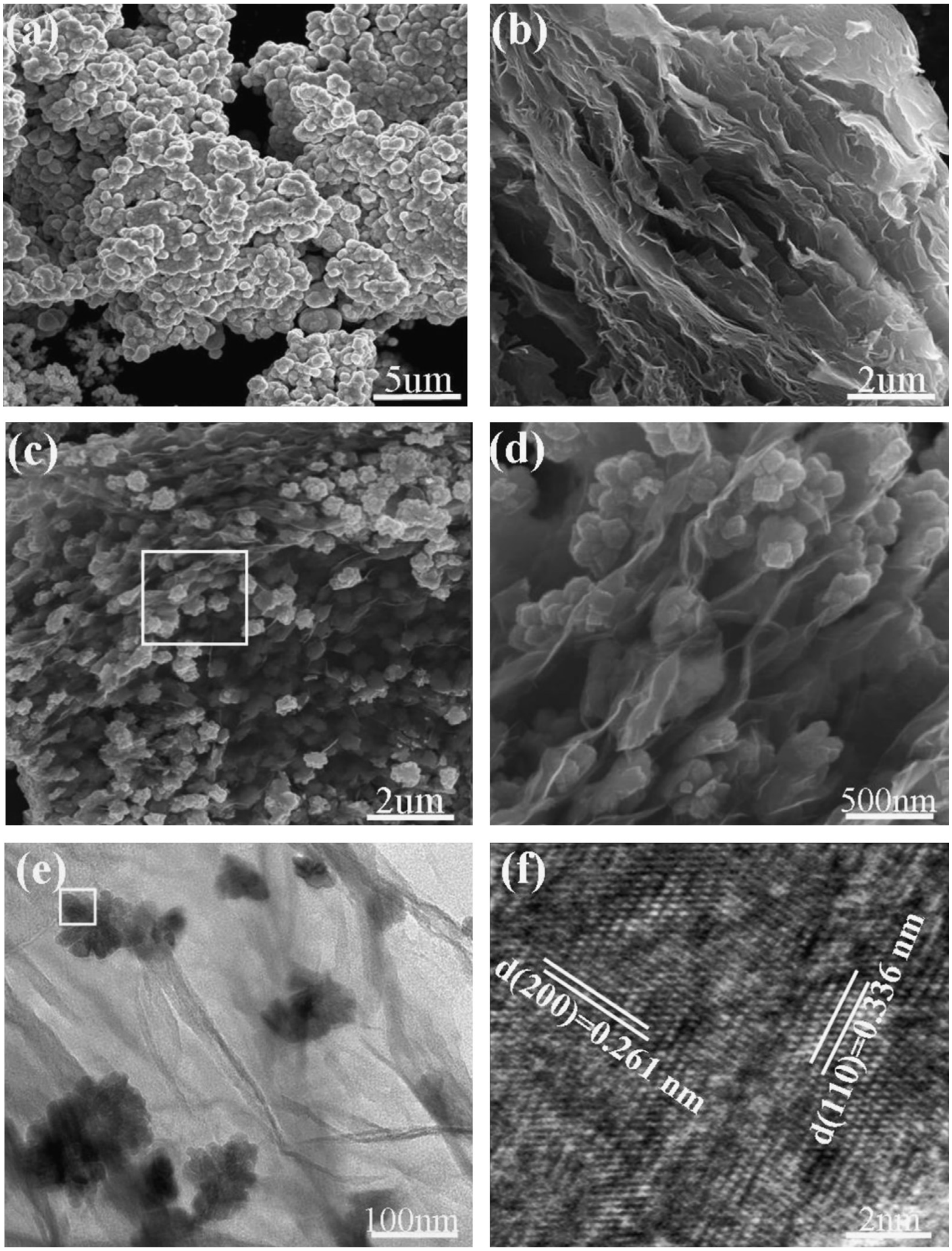

Fig. 2. SEM images of (a) bare SnO_2, (b) graphene oxide, (c) and (d) SnO_2 nano-spheres/graphene composite, (d) TEM image of SnO_2 nano-spheres/graphene composite and (f) HRTEM image of SnO_2.

diameter of 11.38 nm and total pore volume of 0.232 cm^3/g calculated by the Barrett–Joyner–Halenda method [25] (Fig. 3 (a), the insert image). These results prove that the composite has significantly enlarged the surface area and pore volume, which will greatly facilitate the adsorption and transport of Li ion, leading to enhancement in capacity [26].

To evaluate the electrochemical reactivity of the SnO_2 nano-spheres/graphene composites, Fig. 4(a) shows the cyclic voltammetry of the composites. In the first cycle, two obvious peaks appeared in the cathodic process, located around 0.5 −1.0 V and 0.12 V, the broad reduction peak in the range of 0.5−1.0 V corresponds to the conversion of SnO_2 to Sn and formation of Li_2O (Eq. (1)) and a SEI layer as well[27]. The reduction peak around 0.1 V reflects Li−Sn alloying and the lithium ion intercalation into the graphene (Eq. (3)). The equations are as follows[27,28]:

$$SnO_2+4Li^+ + 4e^- \rightarrow Sn + 2Li_2O \quad (1)$$

$$Sn + xLi^+ + xe^- \leftrightarrow Li_xSn(0 \leq x \leq 4.4) \quad (2)$$

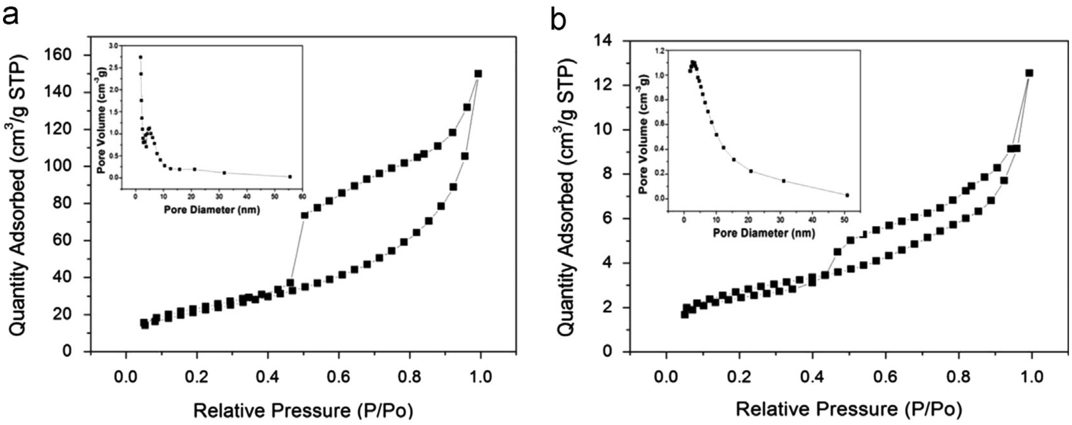

Fig. 3. Isothermal adsorption/desorption curve of (a) SnO_2 nano-spheres/graphene composite and (b) bare SnO_2. The inset shows the pore size distributions curve.

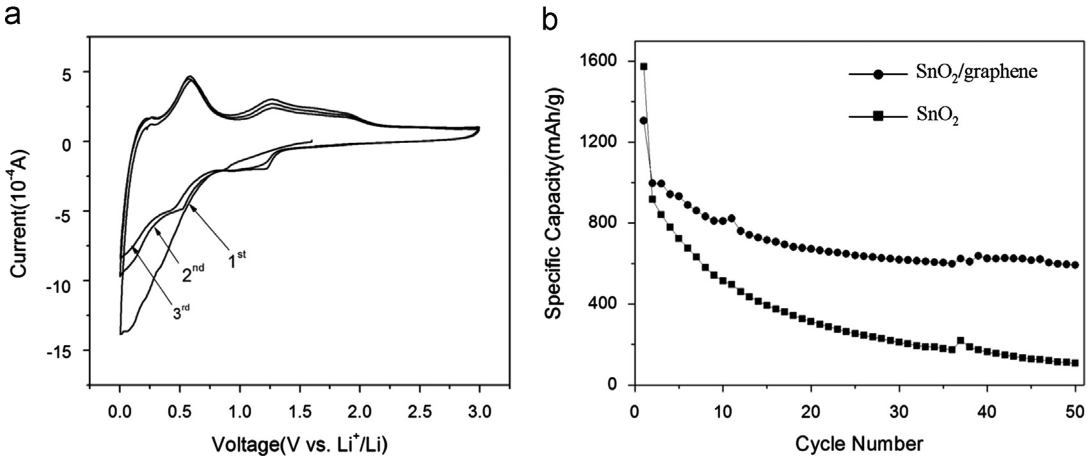

Fig. 4. Electrochemical performance of SnO_2 nano-spheres/graphene composite: (a) Cyclic Voltammetry (CV) and (b) Cycle performance plots of bare SnO_2, and SnO_2 nano-spheres/graphene composite at a current density of 100 mA g^{-1}.

$$C(\text{graphene}) + x\ \text{Li}^+ + x\text{e}^- \leftrightarrow \text{Li}_x\text{C} \tag{3}$$

Two oxidation peaks appear around 0.12 and 0.57 V in the first charge cycle curve. The oxidation peak around 0.12 V can be assigned to the lithium extraction from graphene (Eq. (3)), whereas the weak oxidation peak at 0.57 V is most likely due to dealloying of the Li_xSn (Eq. (2)). The reduction peak currents decreased in the second cycling because of the irreversible reaction and the formation of solid electrolyte inter-face layer.

Cyclic performance of the SnO_2 nano-spheres/graphene hybrids is illustrated in Fig. 4(b) in comparison with that of the pure SnO_2 anode. The SnO_2/graphene composite electrode shows that high initial discharge is 1306 mA h g^{-1}, which maintains a reversible capacity of 594 mA h g^{-1} after 50 cycles. On the other hand, the bare SnO_2 electrode exhibits poor cyclability, retaining only 102 mA h g^{-1} in the 50th cycle. It is well known that SnO_2 anode suffers huge volume change during cycling, resulting in rapid capacity fading. The graphene matrix has a beneficial effect on the enhanced stability of the SnO_2 nano-particles during the Li alloying/de-alloying process. Meanwhile, SnO_2 nano-crystals are tightly attached to the graphene sheets and are spatially separated on the graphene layer. The volume expansion and contraction of SnO_2 nano-spheres can be buffered by the graphene nano-sheets, Meanwhile, SnO_2 nano-spheres/graphene composites with a high specific surface area provide more reaction sites on surface, and its layer by layer structure with lots of pores shorten diffusion length for lithium ions insertion and extraction. Thus, the composite shows an excellent cyclic performance [20,29,30].

4. Conclusion

In summary, a simple hydrothermal method has been designed to synthesize layered SnO_2 nano-spheres/graphene hybrids. FESEM and a high magnification TEM analysis confirmed the uniform attachment of SnO_2 nano-spheres (50–100 nm) on the graphene nano-sheets matrix. Electrochemical performance revealed that the SnO_2 nano-spheres/graphene hybrids anode exhibited much higher reversible capacity and better cycling performance. These improvements could be attributed to the presence of graphene nano-sheets, which suppress the aggregation of active SnO_2 nano-particles, enhance the conductivity of SnO_2, and increase their structural stability during cycling.

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