

Synthesis of Tin Oxide Anchored on Graphene Sheets and its Performance Lithium Storage

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Abstract. The SnO₂/graphene composite has been prepared by a one-step hydrothermal method. The monodisperse SnO₂ nanoparticles of ~3 nm in diameter are not only attached onto the surface of graphene sheets by anchoring with surface functional groups, but they also are encapsulated in pore channels and formed 3D electronic conductive network. The SnO₂/graphene composite exhibits excellent electrochemical performances in lithium-ion batteries through the synergy of the monodisperse SnO₂ and the high specific capacity of graphene sheets. The first discharge/charge capacity is 1843/1244 mA h g⁻¹ at a current density of 100 mA g⁻¹ and the reversible specific capacity remains 698 mA h g⁻¹ after 100 cycles.

Introduction

Lithium-ion batteries (LIBs), as power sources for mobile communication devices, portable electronic devices and electrical vehicles, have been used widely in our life ^[1]. Graphite is the most widely used anode material in commercial LIBs. However it cannot qualify for high capacity batteries because its theoretical lithium storage capacity is only 372 mAh g⁻¹. In order to improve the energy density of batteries, scientists have made great efforts to explore alternative anode materials with higher capacity ^[2]. SnO₂ has attracted much attention as an alternative anode material for rechargeable LIBs. It possesses a specific capacity of 782 mAh g⁻¹, which is much higher than that of traditional graphitic carbon. However a main challenge to its widespread application is the large volume expansion of ~300% induced during the charge/discharge cycles ^[3]. To improve the stability of SnO₂ electrodes and obtain better capacity retention and cycle life for SnO₂, the introduction of carbonaceous materials, such as carbon nanofibers, carbon nanotubes and graphene sheets have been generally accepted due to their high electronic conductivity, excellent buffering effect and mechanical strength ^[4]. Graphene, a one-atom-thick planar sheet of sp²-bonded carbon with a theoretical lithium storage capacity of 744 mA h g⁻¹, high specific surface area (~2600 m² g⁻¹) and excellent electronic conductivity (~6000 S cm⁻¹), has been widely studied for potential application in LIBs because of its unique properties ^[5]. Therefore, much research of SnO₂/graphene composites used as an anode material has been conducted. Recently, several varieties of graphene/SnO₂ nanoparticle composites have been reported as anode materials for LIBs ^[6-11]. These SnO₂/graphene hybrids used as anode for LIBs had different structures and exhibited excellent electrochemical performance. However, an easy and efficient method for synthesizing SnO₂/graphene composite with excellent cycling performance for LIBs should be developed. Herein, we report a one-step hydrothermal method for synthesis of SnO₂/graphene composite with excellent electrochemical performances as an anode material for LIBs.

Experimental

Materials preparation. Graphene oxide (GO) was prepared by a modified Hummers method as we reported previously^[12]. The obtained GO was solved in deionized water, followed by ultrasonic treatment for 60 min. The final suspension of GO was controlled at 1 mg mL⁻¹. The SnO₂/graphene composite was prepared by a one-step hydrothermal. In a typical reaction, a certain quality of SnCl₄·5H₂O was dissolved in 50 mL ethanol, and then added GO aqueous solution, the molar ratio of SnCl₄·5H₂O and GO was 2:1. Adjusted pH value to 10 used ammonia, followed by ultrasonic treatment for 60 min. The suspension solution was transferred to a high pressure reactor and reacted at 160 °C for 15 h. Thus-prepared sample was washed with deionized water and ethanol for several times by centrifugation until the pH value of the filtered solution was 7, and then dried at 80 °C overnight. As comparison, pure SnO₂ was prepared by the same method without the addition of GO.

Materials characterizations. The structures and morphologies of the as-prepared materials were characterized by SEM (QUANTA 200F), TEM (FEI TECNAI G2 F20) and XRD (Bruker D8 Advance with Cu K α radiation) operated at 40 kV and 40 mA.

Electrochemical measurements. Electrochemical measurements were carried out using CR2025 coin-type cells. The working electrode was prepared by coating slurries consisting of the active material, polyvinylidene fluoride and acetylene black with a weight ratio of 80:10:10 in N-methyl-pyrrolidone solvent. The electrolyte was 1 M LiPF₆ dissolved in a mixture of dimethyl carbonate, diethyl carbonate and ethylene carbonate (1:1:1 by weight). Galvanostatic charge-discharge curves of the cells were recorded by a Battery Testing System (Neware Electronic Co., China) at various current densities from 50 to 700 mA h g⁻¹ with the voltage between 3.00 and 0.01 V versus Li⁺/Li at room temperature. Cyclic voltammetry (CV) curves were measured from 0.01 to 3.00 V at a scanning rate of 0.1 mV s⁻¹.

Results and discussion

The crystal structures of the materials were analyzed by XRD. Fig. 1 shows the XRD patterns of GO, pure SnO₂ nanoparticles and SnO₂/graphene composite. The diffraction peak at ~11° can be attributed to (002) of the GO. The diffraction peaks of SnO₂ nanoparticles are clearly distinguishable. All strong diffraction peaks are consistent with tetragonal crystalline SnO₂ phase (JCPDS card no. 41-1445). No diffraction peaks of graphene and GO are observed in the SnO₂/graphene composite, indicating that GO is reduced to graphene, the graphene layer is exfoliated completely and the diffraction peaks of graphene are covered by those of SnO₂^[13]. This observation helps support the inference that GO is reduced in situ by bivalent tin ions.

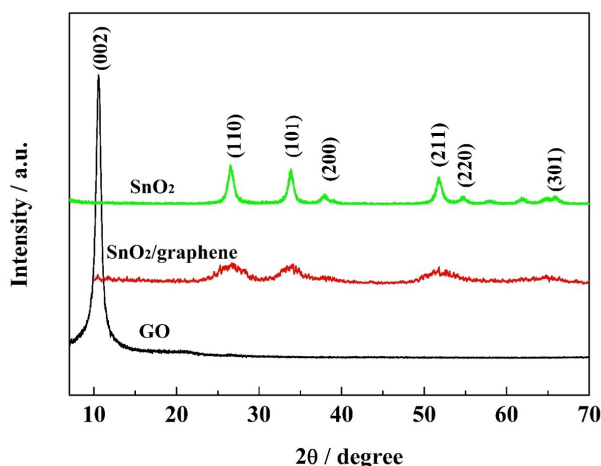


Fig. 1. XRD patterns of GO, pure SnO₂ nanoparticles and SnO₂/graphene composite

The morphologies of GO, SnO₂ and the SnO₂/graphene composite were observed by SEM, TEM and HRTEM. Fig. 2(a) and (b) present the SEM images of GO. It is obvious that the GO are composed of thinner transparent sheets, the area of sheets is larger, and there are many folds. The transparency after

ultrasonic treatment likes a piece of gauze and implies that the GO sheets are only a few layers. Fig. 2(c) shows TEM image of SnO₂ nanoparticles prepared by hydrothermal method, and the average particle diameter of SnO₂ nanoparticles is about 13 nm. The TEM image of SnO₂/graphene composite in Fig. 2(d) reveals that the graphene sheets is decorated with the SnO₂ nanoparticles on the basal plane. The SnO₂ nanoparticles are in the diameters of ~3 nm, uniformly anchored on the surface of graphene sheets, indicating that the GO can prevent the SnO₂ nanoparticles from growing effectively. From the HRTEM images in Fig. 2(e), the interplanar distance of 0.34 can be identified as *d* (110) of SnO₂ nanoparticles. Fig. 2(f) shows the electron diffraction pattern of SnO₂/graphene composite, the four distinct diffraction rings represent (110), (101), (200), and (210) from the rutile phase of SnO₂, confirming the highly crystalline nature of SnO₂ nanoparticles^[14]. The smaller size of SnO₂ nanoparticles and the optimized microstructure of SnO₂/graphene composite are expected to offer a better rate capability of the anode.

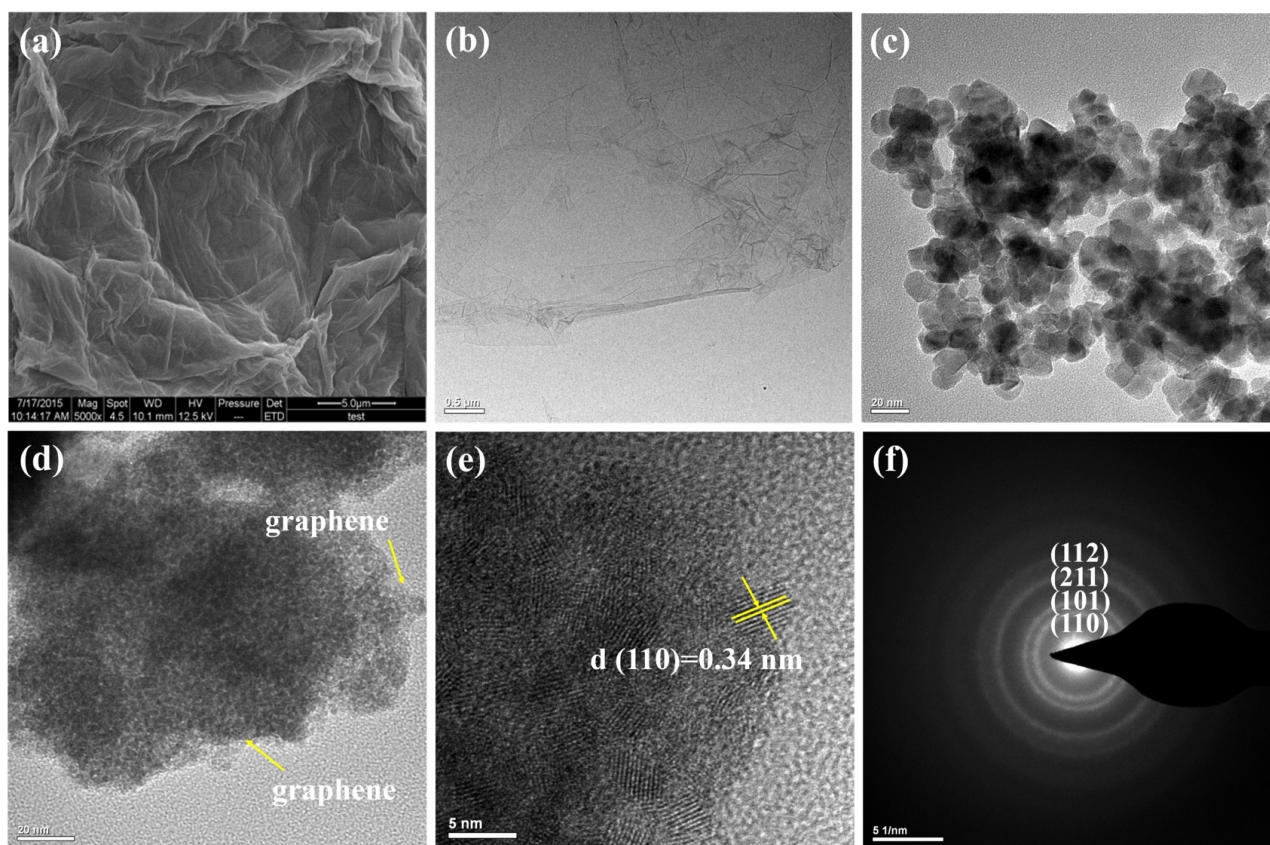


Fig. 2. SEM image of (a) GO, TEM image of (b) GO after ultrasonic treatment, TEM image (c) SnO₂ and (d) SnO₂/graphene, HRTEM images of (e) SnO₂/graphene, and (f) Electron diffraction pattern of SnO₂/graphene

The Li-ion storage behavior of SnO₂/graphene composite was revealed by the CV curve and charge-discharge profiles. Fig. 3(a) shows the CV curves of the first, second and third cycles of the SnO₂/graphene composite at a scan rate of 0.1 mV s⁻¹. In the first cycle, two obvious cathodic peaks appeared around 0.85 and 0.02 V. The peak around 0.85 V is ascribed to the formation of the solid electrolyte interface (SEI) layers on the surface of the active material, the reduction of SnO₂ to Sn. The peak at approximately 0.02 V corresponds to the formation of a series of Li_xSn alloys. In the first anodic process, there is a small peak near 0.17 V, which can be attributed to Li intercalation into graphite to form LiC₆. There are also two obvious plateaus at 0.61 and 1.28 V, which can be ascribed to Li dealloying from Li_xSn and the partially reversible reaction from Sn to SnO₂, respectively. The CV curves clearly elucidated the reversible electrochemical reactions between the lithium ions and the SnO₂/graphene composite in lithium ion batteries. Fig. 3(b) shows the 1st, 2nd and 3rd discharge and charge curves of SnO₂/graphene composite electrode at a current density of 100 mA g⁻¹ in the voltage

range of 3.00~0.01 V vs. Li^+/Li . The potential plateaus observed in the discharge curves are consistent with the CV results, which corresponds to a classical conversion reaction between SnO_2 and Li^+ . In the first cycle, the discharge and charge capacities of $\text{SnO}_2/\text{graphene}$ electrode are approximately 1843 and 1244 mA h g^{-1} with coulomb efficiency of 67.5%. The irreversible capacity loss in the first cycle is attributed to the decomposition of electrolyte forming SEI.

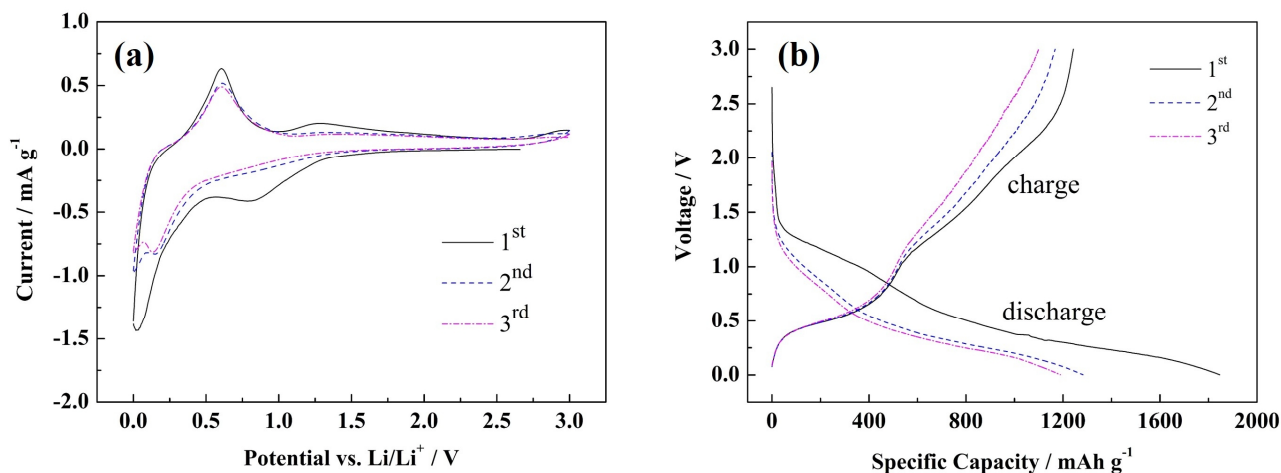


Fig. 3. (a) CV curves of different cycles of $\text{SnO}_2/\text{graphene}$ at a scan rate of 0.1 mV s^{-1} ; (b) Galvanostatic charge-discharge curves of $\text{SnO}_2/\text{graphene}$ at a current density of 100 mA g^{-1}

Fig. 4 shows the cycling performances and rate performance of $\text{SnO}_2/\text{graphene}$ composite electrode. The $\text{SnO}_2/\text{graphene}$ composite electrode demonstrates good cycling performances at different current densities, as shown in Fig. 4(a). The discharge specific capacities are 698, 654 and 587 mA h g^{-1} at current densities of 100, 500 and 700 mA g^{-1} after 100 cycles, respectively. Fig. 4(b) shows the rate performance of $\text{SnO}_2/\text{graphene}$ electrode towards different current densities ($50\sim 700 \text{ mA g}^{-1}$), and reverses back to low current density of 50 mA g^{-1} . With the increases of current density, the reversible specific capacities of $\text{SnO}_2/\text{graphene}$ composite electrode are 1149, 1007, 888, 743, 656, 619, 599, and 570 mA h g^{-1} , respectively. A reversible capacity of 956 mA h g^{-1} is achieved after the current density back to 50 mA g^{-1} . The good rate performance of the $\text{SnO}_2/\text{graphene}$ composite electrode is attributed to the higher electrical conductivity and the special 2D structure of graphene, which not only greatly reduce the intrinsic ohm resistance of the composite electrode, but also facilitate the Li^+ diffusion. In addition, graphene sheets can not only provide a support for dispersing SnO_2 nanoparticles and work as a highly conductive matrix for enabling good contact between them, but also can effectively prevent the volume expansion/contraction and aggregation of SnO_2 nanoparticles during Li charge/discharge process. Thus, it is considered to be a promising anode material of LIBs for the electric vehicles.

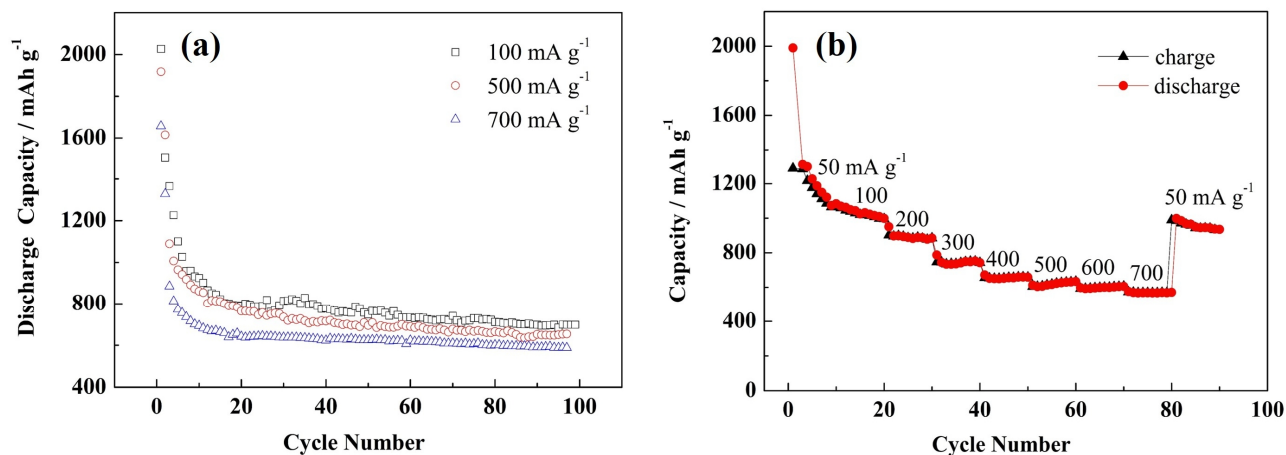


Fig. 4. (a) Cycling performances of $\text{SnO}_2/\text{graphene}$ at 100, 500 and 700 mA g^{-1} ; (b) Rate capability of $\text{SnO}_2/\text{graphene}$ at various current densities from 100 to 700 mA g^{-1}

Conclusions

SnO₂/graphene composite has been synthesized successfully by a one-step hydrothermal method. The preparation method is more simple and controllable. The SnO₂/graphene composite electrode exhibits excellent cycling performances and good rate capability in LIBs. The discharge specific capacity remains 698, 654 and 587 mA h g⁻¹ at current densities of 100, 500 and 700 mA g⁻¹ after 100 cycles, respectively. The excellent electrochemical performances of SnO₂/graphene composite electrode are attributed to the synergy of the monodisperse SnO₂ and the high specific capacity of graphene sheets.

Acknowledgements

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References

- [1] V. Etacheri, R. Marom, R. Elazari, et al, Challenges in the development of advanced Li-ion batteries: a review, *Energy Environ. Sci.* 4 (2011) 3243-3262.
- [2] Wu Z, Zhou G, Yin L, et al, Graphene/metal oxide composite electrode materials for energy storage, *Nano Energy* 1 (2012) 107-131.
- [3] W. Zhang, A review of the electrochemical performance of alloy anodes for lithium-ion batteries, *J. Power Sources* 196 (2010) 13-24.
- [4] J. Chen, X. Lou, SnO₂-based nanomaterials: synthesis and application in lithium-ion batteries, *Small* 9 (2013) 1877-1893.
- [5] P. Guo, H. Song, X. Chen, Electrochemical performance of graphene nanosheets as anode material for lithium-ion batteries, *Electrochem. Commun.* 11 (2009) 1320-1324.
- [6] H. Liu, J. Huang, X. Li, et al, Hydrothermal synthesis and characterization of graphene/self-assembled SnO₂ hybrid, *Physica E* 44 (2012) 1931-1935.
- [7] H. Liu, J. Huang, X. Li, et al, SnO₂ nanorods grown on graphite as a high-capacity anode material for lithium ion batteries, *Ceramics International* 38 (2012) 5145-5149.
- [8] X. Zhou, Y. Yin, L. Wan, et al, A robust composite of SnO₂ hollow nanospheres enwrapped by graphene as a high-capacity anode material for lithium-ion batteries, *J. Mater. Chem.* 22 (2012) 17456-17459.
- [9] J. Zhang, X. Liu, L. Wang, et al, A simple one-pot strategy for the synthesis of ternary reduced graphite oxide/SnO₂/Au hybrid nanomaterials, *Carbon* 49 (2011) 3538-3543.
- [10] B. Zhang, Q. Zheng, Z. Huang, et al, SnO₂-graphene-carbon nanotube mixture for anode material with improved rate capacities, *Carbon* 49 (2011) 4524-4534.
- [11] Y. Yang, R. Pang, X. Zhou, et al, Composites of chemically-reduced graphene oxide sheets and carbon nanospheres with three-dimensional network structure as anode materials for lithium ion batteries, *J. Mater. Chem.* 22 (2012) 23194-23200.
- [12] L. Liu, M. An, P. Yang, J. Zhang, Few-layer graphene prepared via microwave digestion reduction and its electrochemical performances in lithium ion batteries, *Int. J. Electrochem. Sci.* 10 (2015) 1582-1594.
- [13] A. Yang, Y. Xue, Y. Zhang, et al, A simple one-pot synthesis of graphene nanosheet/SnO₂ nanoparticle hybrid nanocomposites and their application for selective and sensitive electrochemical detection of dopamine, *J. Mater. Chem. B* 1 (2013) 1804-1811.
- [14] D. Wang, X. Li, J. Wang, et al, Defect-rich crystalline SnO₂ immobilized on graphene nanosheets with enhanced cycle performance for Li ion batteries, *J. Phys. Chem. C* 116 (2012) 22149-22156.