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Short communication

Green synthesis of SnO_2 nanosheets and their electrochemical properties

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Abstract

The SnO_2 nanosheets were synthesized by a hydrothermal method for high-capacity lithium storage. The products were characterized by XRD, TEM and N_2 adsorption/desorption. The electrochemical performance of SnO_2 nanosheets was measured by galvanostatic charge/discharge cycling. The results show that the SnO_2 nanosheets display superior Li-battery performance with large reversible capacity and good cycling stability.

Keywords: Anode; Lithium ion batteries; SnO_2 nanosheets

1. Introduction

Electrochemical energy storage has been receiving great attention for potential applications in electric vehicles and renewable energy systems from intermittent wind and solar sources. Currently, Li-ion batteries (LIBs) are being considered as the leading candidates for hybrid, plug-in hybrid, and all electrical vehicles, and possibly for utility applications as well [1]. Among LIBs anode materials, SnO_2-based materials have become one of the most promising candidates, as SnO_2 has high theoretical capacity of 782 mAh g^{-1} and low cost [2]. However, its large volume expansion/contraction and severe aggregation associated with the Li-ion insertion and extraction process lead to electrode pulverization, consequently, result in a large irreversible capacity loss and poor cycling stability. To circumvent these problems, SnO_2 with various morphologies, such as nanorods [3], nanotubes [4], nanowires [5] and hollow microspheres [6] have been successfully synthesized. These anode materials have been proven to minimize the severe volume change and exhibit better electrochemical performance, suggesting that structure modification could be a good solution to the poor cyclic retention of SnO_2-based anode materials [7].

Two-dimensional (2D) nanomaterials have attracted a great deal of interest because of their various possibilities in nanoscience and nanotechnology. Significant progress has been reported in the use of nanomaterials as electrode materials for LIBs [8]. In practice, their large surface-to-volume ratio and relatively short diffusion length could enhance the electrochemical as well as kinetic properties. Herein, we report a simple green-chemical method for large-scale synthesis of the 2D SnO_2 nanosheets. In this process, no surface active agents and organic solvents are required. We also demonstrate their promising application as anode materials for LIBs.

2. Experimental

2.1. Preparation and characterization

The SnO_2 nanosheets were prepared by a simple hydrothermal method. In a typical procedure, 4 mmol of $SnCl_2 \cdot 2H_2O$ was dissolved in 20 ml of distilled water and stirred for 20 min to form a homogeneous solution, which was then transferred to a Teflon-lined stainless steel autoclave. After heating in an electrical oven at 200 °C for 16 h, the autoclave was cooled down naturally to room

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temperature. The obtained products were washed with deionized water and ethanol several times and dried at 70 °C.

X-ray diffraction (XRD) pattern was obtained from DMAX-2500PC using Cu/Ka radiation ($\lambda = 1.5406$ Å). Brunauer–Emmet–Teller (BET) specific surface area was measured from N_2 adsorption/desorption using an automatic specific surface area measuring equipment (ASAP 2020M). The morphology of the products was observed by a transmission electron microscope (TEM, LIBRA 200FE).

2.2. Electrochemical measurements

The electrochemical properties of as-prepared products were carried out in coin cells with a Li foil as the counter electrode, active material, carbon black and polyvinylidone difluoride (PVDF) binder in the weight ratio of 80:10:10 as the working electrode, 1 M $LiPF_6$ in the volume ratio of 1:1 ethyl methyl carbon (EMC)/dimethyl carbonate (DMC) as the electrolyte. The cells were galvanostatically charge–discharged in the voltage range 0–3.0 V vs. Li/Li^+ at a current density of 100 mA g^{-1} via a Battery Testing System (Ningbo baite testing equipment Co., China).

3. Results and discussion

The typical XRD pattern of the as-obtained SnO_2 nanosheets after the hydrothermal treatment is shown in Fig. 1(a). All the broad diffraction peaks of XRD pattern are in accordance with the tetragonal rutile SnO_2 structure with $a = 4.738$ Å and $c = 3.188$ Å (JCPDS 41–1445).

The morphology of the SnO_2 nanosheets was observed by TEM in Fig. 1(b). It can be clearly seen that the product consisted of well distributed SnO_2 two-dimensional structures with open and flat surface. The edge length of the SnO_2 nanostructures is about 20–70 nm in both dimensions. The thickness of nanosheets cannot be measured accurately from this TEM image. In the HRTEM image (Fig. 1(b), inset) of a single nanoplate, the lattice fringes have an interplanar spacing of 3.37 Å, which agrees with the d value of the (110).

The N_2 adsorption/desorption isotherms of the as-prepared products are shown in Fig. 1(c). The SnO_2 nanosheets possess 69.0 $m^2\ g^{-1}$ of specific surface area, which is higher than that of the SnO_2 nanotubes (53.2 $m^2\ g^{-1}$) [9] synthesized via a mild solution chemical route and much higher than that of the flower-like SnO_2 (1.3 $m^2\ g^{-1}$) [10] prepared by the hydrothermal method. The total pore volume of the SnO_2 material, obtained here, is about 0.2 $cm^3\ g^{-1}$. The average pore diameter is about 11.3 nm calculated by the BET model.

The electrochemical performance of the as-prepared SnO_2 nanosheets was evaluated by galvanostatic charge/discharge cycling at the current density of 100 mA g^{-1} in a voltage range from 0 to 3.0 V. Fig. 1(d) shows that the SnO_2 nanosheets deliver a lithium insertion capacity of 1508 mAh g^{-1} and a charging capacity of 1053 mAh g^{-1} with coulombic efficiency of 69.8% in the first cycle. The initial capacity loss may result from the incomplete conversion reaction and irreversible lithium loss due to the formation of a solid electrolyte interphase (SEI) layer [7]. From the second cycle, coulombic efficiency is improved significantly. More importantly, the charge/discharge

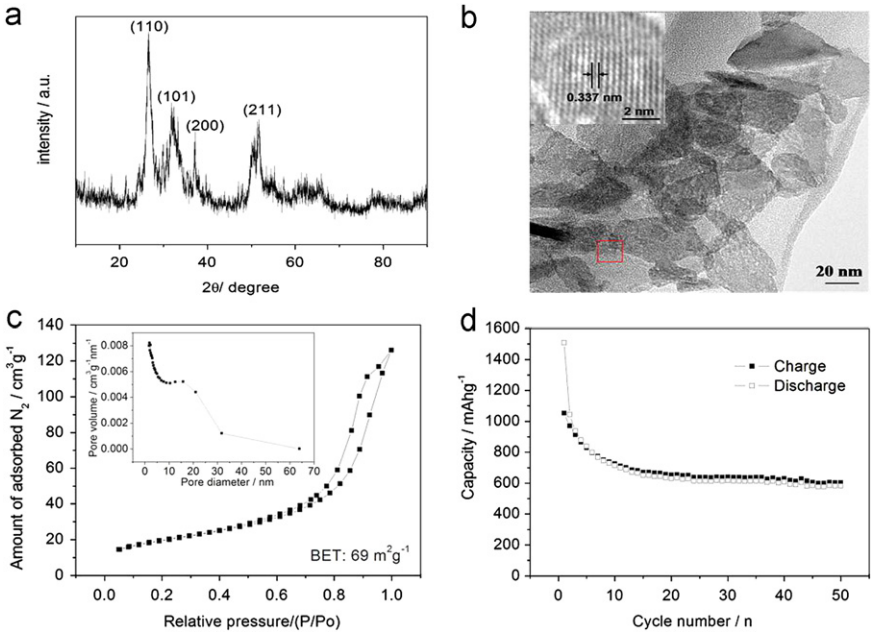

Fig. 1. (a) XRD pattern of the SnO_2 nanosheets, (b) TEM image of the SnO_2 nanosheets, inset shows HRTEM image of the SnO_2 nanosheets, (c) nitrogen adsorption/desorption isotherms of the SnO_2 nanosheets, inset shows the porosity distribution, and (d) Cycle performances of the SnO_2 nanosheets at a current density of 100 mA g^{-1}.

capacity becomes very stable after 25 cycles and the electrode could retain a reversible capacity of 604 mAh g^{-1} after 50 cycles at the current density of 100 mA g^{-1}. The average capacity fading of the SnO_2 nanosheets is 0.77% (2nd–50th) and 0.21% (25th–50th) per cycle. In comparison, the average capacity fading of the nanowires, nanotubes and nanopowders are estimated to be 1.45%, 1.87% and 3.46%, respectively, per cycle after the second cycle [11], which were much higher than that of our SnO_2 nanosheets.

4. Conclusions

In summary, we have developed a simple and effective strategy to fabricate the SnO_2 nanosheets via a hydrothermal method. The as-obtained product possesses high BET surface area and pore volume. The SnO_2 nanosheets exhibit a superior lithium storage capacity and cycle performance, indicating their promising potential as a novel anode material for high-performance LIBs.

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