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Ultrathin SnO nanosheets as anode materials for rechargeable lithium-ion batteries

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ABSTRACT

SnO ultrathin nanosheets with a highly pure crystal phase were successfully prepared via a simple and effective hydrothermal process, using tin dichloride dihydrate ($SnCl_2 \cdot 2H_2O$) as a stannous source in the presence of hexamethylenetetramine (HMT). SEM and TEM images showed that the obtained SnO products are uniform and ultrathin nanosheets. The electrochemical properties results indicated that the obtained SnO nanosheets exhibited excellent discharge capacity, the reversible capacity was 559 mAh g^{-1} after 20 cycles, and the SnO nanosheets retain high capacity even at high discharge current densities. The enhanced performance was attributed to the unique structure of ultrathin SnO nanosheets and highly pure crystal phase.

1. Introduction

Graphite is the widely used commercial anode material for rechargeable lithium-ion batteries, but its theoretical specific capacity is only 372 mAh g^{-1}, which cannot meet the increasing demand for high performance lithium-ion batteries. Great efforts have been devoted to develop different types of materials with high reversible capacity, long cycle life, and low cost [1,2]. Among the materials, SnO is regarded as one of the most promising candidate for anode materials owing to its high theoretically gravimetric lithium storage capacity and low potential of lithium ion intercalation [3]. Unfortunately, tin-based materials have a disadvantage, in that they undergo a significant volume expansion and contraction during Li^+ insertion and extraction. This causes cracking and crumbling, resulting in “dead volume”, which is electrically disconnected from the current collector, and results in subsequent degradation of electrode performance during cycling [4]. Therefore, the tailoring of nanostructure has become a critical process in developing electrode materials to alleviate the volume changes and mechanical stress. As we know, SnO nanocrystals are very difficult to be synthesized due to their easy transformation into SnO_2 by oxidization. Although some successful approaches have been reported for the preparation of SnO crystals with various morphologies, such as nanowires [5,6], nanoribbons [7], nanosheets [8,9], and diskettes [10]. However, these structures are of large size, tedious synthetic procedures, and/or low battery capacity, which further hinder their large-scale industrial applications.

Herein, we present a facile one-step method for mass production of the ultrathin SnO nanosheets with highly pure crystal phase by using $SnCl_2 \cdot 2H_2O$ and HMT as the precursors. The electrochemical properties of the products were studied. According to the experimental results, a possible Li^+ insertion/extraction mechanism of the SnO anode materials was also discussed.

2. Experimental

All chemicals were of analytical grade and used without further purification. Typically, 0.4513 g $SnCl_2 \cdot 2H_2O$ and 0.8411 g HMT were dissolved in 30 mL deionized water with vigorous stirring for 1 h to form a homogeneous solution, and then added 30 mL n-butanol dropwise into the above solution. Subsequently, the reaction mixture was transferred into a Teflon-lined stainless steel autoclave and kept at 160 °C for 24 h. Afterwards, the autoclave was cooled naturally down to room temperature. The precipitates were collected by centrifugation, washed several times with deionized water and ethanol, respectively, and dried at 80 °C for 12 h in vacuum. The products were characterized with an X-ray diffraction (XRD, RigaKu D/max-2550), a scanning electron microscope (SEM, JEOL JSM-6700F), a transmission electron microscope

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(TEM, JEOL JEM-200CX) and a high-resolution transmission electron microscope (HRTEM, JEOL JEM-2010F), energy dispersive X-ray spectroscopy (EDS, OXFORD INCA), FT-IR (Nicolet AVATAR 370), thermogravimetric (TG, NETZSCH STA 409 PC/4/H), and N_2 sorption isotherms (BET, Quadrasorb SI).

Electrochemical properties: For the electrochemical measurement, the active materials (SnO, 70 wt%) and carbon black conductive additives (Super-P, 20 wt%) were mixed and rolled with polytetrafluoroethylene (PTFE, 10 wt%) powder to form a film. The obtained film was pressed onto a copper mesh and dried under vacuum for 12 h at 80 °C. The electrolyte used was 1 M $LiPF_6$ dissolved in dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethylene carbonate (EC) (1:1:1 by weight). Cyclic voltammetry was performed on an AUTOLAB electrochemical workstation using the above-mentioned cell in the voltage range of 3–0.005 V (vs Li/Li^+) at a sweep rate of 0.2 mV s^{-1}. Discharge/charge testing was carried out on Land-CT2001A battery test system between 0.005 V and 3.0 V with a constant current density of 100 mA g^{-1}. All the electrochemical tests were carried out at room temperature.

3. Results and discussion

Fig. 1a and b shows the SEM and TEM images of the obtained SnO products, respectively. Clearly, the morphologies of SnO ultrathin nanosheets are disorderly accumulated on a large scale. Seen from Fig. 1c, an HRTEM image confirmed that the prepared SnO was highly crystalline with the lattice spacing of 0.299 nm, corresponding to (101) planes of romarchite SnO. The EDS results in Fig. 1d show the intense peaks of Sn and O, indicating that the composition of products are only Sn and O elements, and while the Cu and C signals are derived from the supporting TEM grid. Meanwhile, the EDS analysis gives an average Sn/O composition of 1:1 within the accuracy of the technique, in good accordance with the stoichiometry of SnO.

Fig. 2a illustrates the typical XRD pattern, and all the peaks can be well indexed to the tetragonal SnO structure (JCPDS No: 06–0395). Fig. 2b shows the FT-IR spectra of the SnO nanosheets. Obviously, the absorption band at 513 cm^{-1} can be attributed to stretching vibrations of Sn–O in the SnO nanosheets [6]. In the TG curves shown in (Fig. 2c), the loss of weight up to 100 °C was caused by the residual water molecule and the weight increased around 300 °C results from the oxidation of SnO to SnO_2. The N_2 sorption isotherm was shown in Fig. 2d, the prepared SnO products exhibited a hysteresis hoop at high relative pressure, suggesting the existence of mesopores in the material [11]. The obtained SnO has a BET surface area of 51.4 $m^2\,g^{-1}$.

The electrochemical reaction of SnO with lithium-ion is generally described as follows [12]:

$$SnO + 2Li^+ + 2e^- \rightarrow Sn + Li_0O \quad (1)$$

$$Li^+ + e^- + \text{electrolyte} \rightarrow SEI\ (Li) \quad (2)$$

$$Sn + xLi^+ + xe^- \leftrightarrow Li_xSn\ (0 \le x \le 4.4) \quad (3)$$

Fig. 3a shows the cyclic voltammograms of SnO sample. In the first cyclic voltammogram, the cathodic peaks at the potential of 1.15 V and 0.74 V can be attributed to the decomposition of SnO to Sn and Li_2O composite (Eq. (1)) and formation of solid electrolyte interphase (SEI, Eq. (2)), respectively. Moreover, these two processes are believed to be irreversible. A pair of cathodic and anodic peaks at 0.07 and 0.71 V can be ascribed to the reversible alloying and de-alloying reaction of Li_xSn (Eq. (3)). The results are similar to those reported by other groups [9]. The properties of the SnO nanosheets as an anode material for a rechargeable lithium-ion battery were studied using constant current discharge/charge measurements as shown in Fig. 3b. The first discharge capacity is very high, which is 1496 mAh g^{-1}, and the observed capacity during the first charge is 1016 mAh g^{-1}, corresponding to the coulombic efficiency which is 67.9%. From Fig. 3b, the 5th discharge and charge capacities are determined as 882 and 829.4 mAh g^{-1},

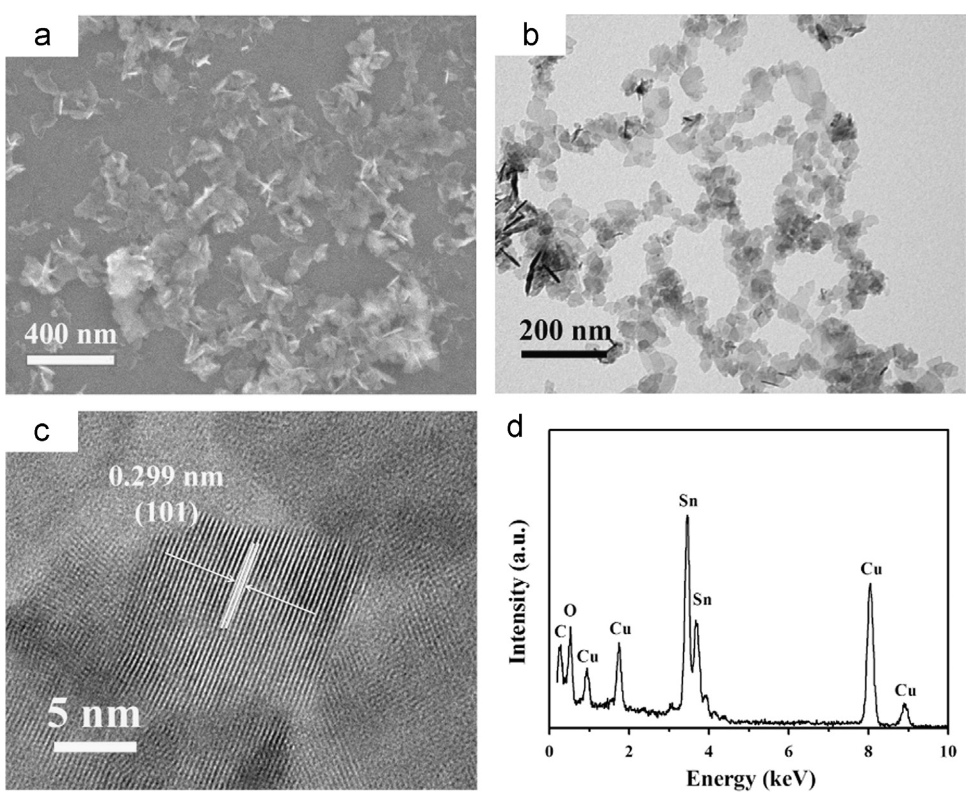

Fig. 1. SEM image (a), TEM image (b), HRTEM image (c), and EDS spectrum (d) of the SnO nanosheets.