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Synthesis of amorphous $ZnSnO_3$ hollow nanoboxes and their lithium storage properties

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ABSTRACT

Amorphous $ZnSnO_3$ hollow nanoboxes were synthesized for the first time in a large scale by a facile alkaline solution etching method. Specifically, solid and hollow nanocubes of precursor $ZnSn(OH)_6$ were first prepared successively with controllable amounts of alkali. $ZnSnO_3$ hollow nanoboxes with amorphous phase were obtained after calcination of the hollow precursors, and they well inherited the hollow morphology of the precursors. As an anode material for lithium-ion batteries, the synthesized $ZnSnO_3$ hollow nanoboxes had a high initial reversible capacity of 661 mA h g^{-1} at 0.1 A g^{-1} rate and acceptable rate performance. These good performances can be attributed to the hollow nanostructures that accommodate the large volume change during the alloying–dealloying process.

1. Introduction

Hollow nanostructure, as a famous family of functional materials, has attracted considerable attention in recent years due to its high surface areas and the internal void space [1–5]. The obtained hollow morphology is almost spherical by conventional templated synthesis. Recently, many efforts have been made to obtain non-spherical hollow morphologies through chemical etching [6], the Kirkendall diffusion [7], galvanic replacement [8], and self-templating [9]. Zinc stannate nanostructures, as one of ternary metal oxides, including nanowires, nanocubes, and nanosheets, have been synthesized and investigated for wide applications such as catalysts, phonics, sensors, piezoelectric, pyroelectric, and lithium ion batteries (LIBs) [10–13]. Recently, Zang et al. have fabricated $ZnSnO_3$ hierarchical nanocages via a solution synthetic method [14]; Hu et al. have prepared zinc stannate solid and hollow microcrystals via hydrothermal procedure and the subsequent acid etching methods [15], and Wang et al. have prepared solid cube-like $ZnSnO_3$ mesocrystals by dual-hydrolysis-assisted liquid precipitation and subsequent hydrothermal route [12].

In this study, we obtained amorphous $ZnSnO_3$ hollow nanoboxes in a large scale by a facile alkaline etching method. Specifically, solid and hollow nanocubes of $ZnSn(OH)_6$ precursors were prepared successively with controllable amounts of alkali, and then the $ZnSnO_3$ hollow nanoboxes were obtained by a simple calcination of the hollow precursors, which well inherited the hollow morphology of the precursors. We also evaluated the lithium-storage performance of the as-prepared $ZnSnO_3$ hollow nanoboxes as an anode material for LIBs. The corresponding electrode has a high initial reversible capacity of 661 mA h g^{-1} at 0.1 A g^{-1} rate and acceptable rate performance due to the hollow structure could alleviate the stress and volume changes during the lithiation/delithiation process.

2. Experimental section

Synthesis of $ZnSnO_3$ hollow nanoboxes was done as follows. First, a mixed aqueous solution of $C_6H_8O_7 \cdot H_2O$ (0.42 g, 2 mmol) and $ZnCl_2 \cdot 5H_2O$ (0.452 g, 2 mmol) in water (20 mL) was added to a solution of $SnCl_4 \cdot H_2O$ (0.557 g, 2 mmol) in anhydrous ethanol (10 mL) under stirring, and then solid NaOH (0.816 g, 20.4 mmol) was directly added into the above mixture solution. Subsequently, 50 mL distilled water was added; thus the solid nanocubes $ZnSn(OH)_6$ precursor solution was obtained. Second, 40 mL 2.0 M NaOH solution was dropped into the precursor solution with stirring. After centrifugation and washing with distilled water and ethanol several times, $ZnSn(OH)_6$ hollow nanoboxes precursor was obtained under 80 °C drying. Finally, the above hollow $ZnSn(OH)_6$ precursor was annealed in N_2 flow at 500 °C for 2 h with a heating rate of 1 °C min^{-1} to obtain the $ZnSnO_3$ hollow nanoboxes. The obtained samples were investigated by X-ray

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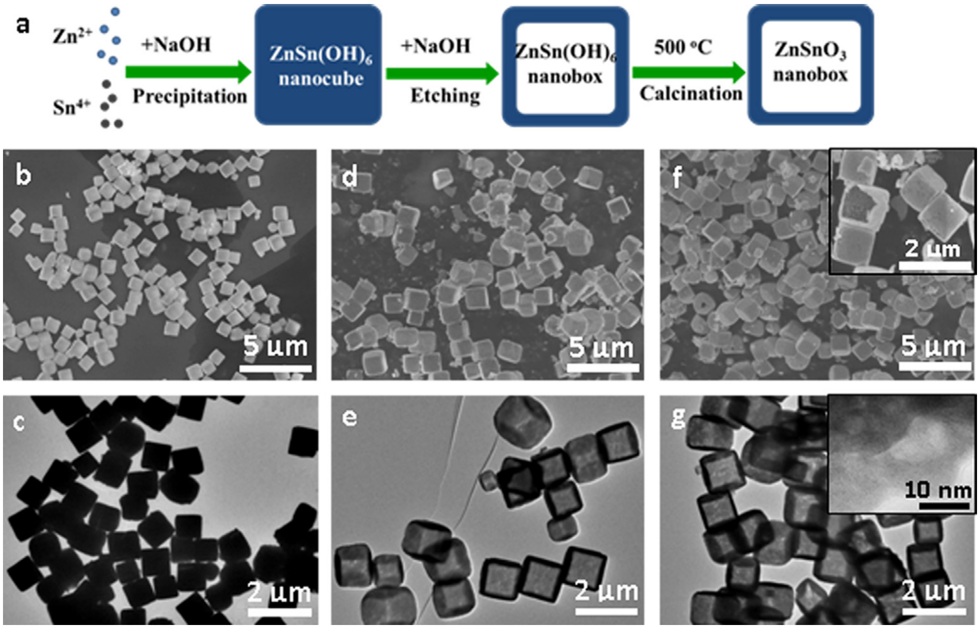

Fig. 1. (a) Schematic representation of the synthesis progress of the $ZnSnO_3$ hollow nanoboxes. The corresponding SEM and TEM images of (b, c) $ZnSn(OH)_6$ solid nanocubes, (d, e) $ZnSn(OH)_6$ hollow nanoboxes, and (f, g) $ZnSnO_3$ hollow nanoboxes. Insets in (f, g) show magnified TEM images.

diffraction (Philips X'pert Pro X-ray diffractometer), scanning electron microscopy (SEM, Hitachi S-4800), and transmission electron microscopy (TEM, JEOL, JEM 2100). Electrochemical measurements were performed using 2032 type coin cells. The working electrode consisted of active material, conducting carbon and polyvinyldifluoride (PVDF) in a weigh of 7:2:1 dissolved in N-methylpyrrolidone (NMP). The above slurry was coated onto a copper foil current collector and dried in vacuum at 110 °C. The electrolyte is 1 M $LiPF_6$ in an ethylene carbonate and diethyl carbonate (EC/DMC, 1:1 volume) mixture, and Celgard 2500 separator was used. Coin cells were assembled in an argon-filled glove-box and Li foil was taken as the counter-electrode. Galvanostatic charge–discharge experiments were performed in the range of 0.01–3.00 V at different current densities using a battery test system (LAND, Wuhan Jinnuo Electronics Ltd.).

3. Results and discussions

Fig. 1 shows the schematic synthetic process and the corresponding SEM and TEM images observation of the $ZnSnO_3$ hollow nanoboxes. As schematically illustrated in Fig. 1a, the solid and hollow nanocubes of precursor $ZnSn(OH)_6$ were first prepared successively by an alkali etching progress, and then $ZnSnO_3$ hollow nanoboxes were obtained by a simple calcination of the precursor. From the SEM and TEM images in Fig. 1b–g, we could clearly know that there is a distinct boundary between the translucent center and dark edge in the TEM images for the hollow structure, while dark was well-distributed for the solid precursor $ZnSn(OH)_6$. The large-scale monodisperse $ZnSnO_3$ hollow nanoboxes inherits from the morphology of the hollow $ZnSn(OH)_6$ precursor after calcination that derives from the controllable amounts alkali etching. The as-prepared $ZnSnO_3$ with an average edge length of 1.0 μm and a wall thickness between 20 and 30 nm does not have structural collapse. One cracked cube in the magnified SEM image (inset of Fig. 1f) further demonstrates the presence of hollow morphology. Recently, Straumal et al. investigated the effect of grain boundaries on ferromagnetism of nanograined oxide or “magnetic” atoms-doped oxide in detail, which depend on the grain size, amorphous surficial, interfacial, and concentration of “magnetic” atoms [16,17]. Fig. 1f and g demonstrates the samples with developed grain boundaries and free surfaces, which could improve the ferromagnetic properties of this type of $ZnSnO_3$; specific work remains to be further studied.

Fig. 2a shows the XRD patterns of the as-prepared $ZnSn(OH)_6$ precursor and $ZnSnO_3$ product. All the sharp diffraction peaks can be assigned to pure $ZnSn(OH)_6$ cubic structure (Pn-3(201), $a=b=c=7.8$, JCPDS no. 73-2384). No signals from possible impurities such as $Zn(OH)_2$ or SnO_2 were detected due to the stoichiometrically controlled co-precipitation of Zn^{2+} and Sn^{2+} in the excess alkaline solution. For the $ZnSnO_3$ product, there are no sharp diffraction peaks, and this result indicates that the structure of the product was amorphous, which was also confirmed by the high resolution TEM image taken on the edge area of an individual (inset of Fig. 1g). In addition, the energy-dispersive X-ray (EDX) spectrum confirms the existence of Zn, Sn, and O elements, while Cu signal comes from the substrate (Fig. 2b). The XPS spectrum further confirms that the sample mainly contains Zn, Sn, and O (Fig. 2c). The peaks at 1022.1 and 1045.2 eV is assigned to Zn $2p_{3/2}$ and Zn $2p_{1/2}$ for the Zn^{2+} state, respectively. The two peaks at around 495.1 and 486.9 eV are assigned to Sn $3d_{3/2}$ and Sn $3d_{5/2}$ of Sn^{4+} ion, respectively, and the peak at 530.5 eV corresponds to the binding energy of the O 1s (Fig. 2d) consistent with the previous study [2]. The ration of Zn:Sn:O of 12.89:12.95:43.87 is given by the quantification of peaks, indicating that the molar ratio of Zn to Sn to O is near 1:1:3.

The lithium storage performances of the $ZnSnO_3$ hollow nanoboxes were evaluated as shown in Fig. 3. Fig. 3a shows the galvanostatic charge/discharge curves at a current density of 0.1 A g^{-1} and the initial discharge and charge capacity is 1266 and 661 mA h g^{-1}, respectively. The large initial irreversible capacity derives from the formation of the solid electrolyte interface (SEI) in the first discharge process. Fig. 3b illustrates the capacities and Coulombic efficiency with the prolonged cycle, showing that a high Coulombic efficiency above 95% could be obtained. As shown in Fig. 3c and d, the $ZnSnO_3$ hollow nanoboxes show acceptable rate capability with increasing current density. In comparison with the reported $ZnSnO_3$ solid nanocubes