Research Article
A Rational Self-Sacrificing Template Route to LiMn$_2$O$_4$ Nanotubes and Nanowires

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Single-crystalline LiMn$_2$O$_4$ nanotubes and nanowires have been synthesized via a low-temperature molten salt synthesis method, using the prepared $\beta$-MnO$_2$ nanotubes and $\alpha$-MnO$_2$ nanowires as the precursors and self-sacrificing template. The materials were investigated by a variety of techniques, including X-ray powder diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), and high-resolution transmission electron microscopy (HRTEM). The results indicate that the prepared LiMn$_2$O$_4$ nanotube and nanowire samples are both spinel phase, have lengths up to several micrometers and diameters of hundreds and tens of nanometers, respectively.

1. Introduction

One-dimensional (1D) nanomaterials, with their large surface areas and possible quantum confinement effects, exhibit distinct electronic, optical, chemical, and thermal properties [1]. Nanotubes and nanowires are always the focus of study of 1D nanomaterials, so the exploration of simple synthetic methods that can be generalized is a significant challenging field [2].

In recent years, the self-sacrificing template synthesis has been proved to be a facile and efficient route to nanotubes [3–6] and nanowires [7–9]. The idea of converting nanostructures of manganese dioxide to lithium manganese oxide has been described by several groups [10–15]. A sol-gel-AAO or polycarbonate membrane template strategy was used to synthesize LiMn$_2$O$_4$ nanotubes by Li et al. [16] and Li et al. [17] and LiMn$_2$O$_4$ nanowires by Zhou et al. [18] and Liu et al. [19]; an electrospinning technique was also utilized to prepare LiMn$_2$O$_4$ nanowires by Yu et al. [20] and Fu et al. [21]. Hosono et al. [22] reported a high temperature molten salt reaction to prepare LiMn$_2$O$_4$ nanowires at 450°C, using the prepared Na$_{0.44}$MnO$_2$ nanowires as a self-sacrificing template and converting Na$_{0.44}$MnO$_2$ nanowires to LiMn$_2$O$_4$ nanowires. However, to the best of our knowledge, a simple route to 1D LiMn$_2$O$_4$ nanotubes and nanowires at low temperature has still rarely been reported. Herein, we report a low-temperature molten salt route to synthesize LiMn$_2$O$_4$ nanotubes and nanowires, using the prepared $\beta$-MnO$_2$ nanotubes and $\alpha$-MnO$_2$ nanowires as self-sacrificing templates.

2. Experimental Section

2.1. Synthesis Procedures. The precursor $\beta$-MnO$_2$ nanotubes were prepared following a procedure found in the literature [23]. In a typical process, 4 mmol of MnSO$_4$·H$_2$O was dissolved in 10 mL of distilled water, and 4.5 mmol of PVP (K30, polymerization degree 360) was added slowly to it with vigorous stirring. When the solution clarified, 8 mL of aqueous solution containing 8 mmol of NaClO$_3$ was added to the above solution under continuous stirring. The resulting transparent solution was then transferred into a Teflon-lined stainless steel autoclave (20 mL) of 70% capacity of the total volume. The autoclave was sealed and maintained at 160°C for 10 h. After the reaction was completed, the autoclave was allowed to cool to room temperature naturally. The solid black precipitate was filtered, washed several times with...
distilled water and absolute ethanol to remove impurities, and then dried at 50°C for 4 h.

The precursor α-MnO2 nanowires were synthesized using the technique reported previously in [24]. In a typical process, 0.008 mol MnSO4·H2O, 0.02 mol (NH4)2SO4, and 0.008 mol (NH4)2S2O8 were put into distilled water at room temperature to form a homogeneous solution, which was then transferred into a 40 mL Teflon-lined stainless steel autoclave, sealed, and maintained at 140°C for 12 h. After the reaction was completed, the resulting solid products were filtered, washed with distilled water to remove the remnant ions, and finally dried at 60°C for 4 h.

For the synthesis of LiMn2O4 nanotubes (noted as sample 1) and nanowires (noted as sample 2), 0.59 LiNO3–0.41 LiOH flux (melting point = 183°C) were used as lithium salts [25]. In a typical experimental procedure, 10 mmol MnO2 powders (β-MnO2 nanotubes or α-MnO2 nanowires) and an appropriate amount (for example 100 mmol) of the flux were firstly mixed with a mortar and pestle, heated at ~230°C for ~10 h in air, and then air-cooled to room temperature. The resulting products were collected, washed repeatedly with distilled water, filtered, and finally dried in an oven at 60°C for 4 h.

2.2. Characterization. The samples were characterized by X-ray powder diffraction (XRD), which was recorded on a Japan Rigaku Dmax-γA X-ray powder diffractometer with graphite-monochromatized Cu-Kα radiation (λ = 0.154056 nm). The transmission electron microscopy (TEM) images and selected-area electron diffraction (SAED) pattern were captured on a Hitachi Model H-800 instrument at an acceleration voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) images and Energy-dispersive X-ray spectrum (EDS) were obtained with a JEOL-2010 transmission electron microscope, employing an accelerating voltage of 200 kV. Field-emission scanning electron microscope (FESEM) images were taken on a field-emission microscope (JEOL JSM-6700F, 5 kV).

3. Results and Discussions

Figures 1(a) and 1(b) show the typical XRD patterns of sample 1 and sample 2. All of the intensive and sharp peaks can be readily indexed to the pure spinel structure of crystalline LiMn2O4 [space group: Fd3m] (JCPDS 35-782).

TEM and FESEM images of the precursor MnO2 nanotubes (Figures 2(a) and 2(e)) and nanowires (Figures 2(c) and 2(g)) indicate that the morphology and size of the prepared precursors are in good agreement with those in the studies in [23, 24]. Figures 2(b) and 2(f) show TEM and FESEM images of sample 1, from which, one can see that these LiMn2O4 nanotubes have diameters of hundreds of nanometers and lengths up to several micrometers, basically retain the morphology of the precursor MnO2 nanotubes. Figures 2(d) and 2(h) show TEM and FESEM images of sample 2, which reveal that the LiMn2O4 nanowires have diameters of tens of nanometers and lengths up to several micrometers, and the morphology of the precursor MnO2 nanowires is also mainly maintained. The above phenomenon suggests that the precursor MnO2 nanotubes and nanowires may serve as self-sacrificing template for the formation of LiMn2O4 nanotubes and nanowires.

We have also characterized the as-synthesized LiMn2O4 nanotubes and nanowires using HRTEM, SAED, and EDS. A representative HRTEM image of a section of a single nanotube is shown in Figure 3(a). The discriminable lattice fringes illustrate that the prepared LiMn2O4 nanotubes are single crystals in the area shown. The lattice fringes, parallel to the axial direction of the nanotube, have spacing of 0.475 nm, which match well with the separations between the neighboring lattices of the (111) planes of cubic LiMn2O4. This result indicates that the LiMn2O4 nanotube has preferential growth direction perpendicular to [111] direction. The clear and symmetrical spots in the corresponding SAED pattern also indicate that the single nanotube is single-crystalline in nature. The composition of the sample as calculated from the EDS analysis (Figure 3(b))
Figure 2: Typical TEM images of precursor MnO$_2$ nanotubes and nanowires (a and c) and sample 1 and 2 (b and d), FESEM images of precursor MnO$_2$ nanotubes and nanowires (e and g) and sample 1 and 2 (f and h).

gives an Mn : O atomic ratio of 1 : 2.08, which is close to the stoichiometry of LiMn$_2$O$_4$. The HRTEM image (Figure 3(c)) taken from a single wire shows two sets of distinct fringe spacings of ca. 0.477 and 0.291 nm that match well with the separation between the (111) and (220) lattice planes of cubic LiMn$_2$O$_4$, respectively, which indicate that the growth direction of the wire is along [110] direction. The inset SAED pattern of the nanowire was recorded with the electron beam along the [T12] zone axis. It also demonstrates that this nanowire is single crystal and may have a growth direction of [110]. The composition of the nanowires as calculated from the EDS spectrum (Figure 3(d)) gives an Mn : O atomic ratio of 1 : 2.07, which is close to the stoichiometry of LiMn$_2$O$_4$.

The specific formation mechanism of the LiMn$_2$O$_4$ nanotubes and nanowires is not yet clear and warrants further investigation. Concerning the formation mechanisms for nanotubes and nanowires, we think that converting nanostructures of manganese dioxide to lithium manganese oxide is based on a lithiation reaction [10–12], and the 1D tubes and wires can be mainly retained in the present synthetic conditions.

The net lithiation reaction might be simply formulated by:

$$4\text{MnO}_2 \ (\text{tube or wire}) + 2\text{LiNO}_3 = 2\text{NO}_2 + \text{O}_2 + 2\text{LiMn}_2\text{O}_4 \ (\text{tube or wire}). \quad (1)$$

Xia et al. believe that the formation of Ag$_2$Se nanowires from Se nanowires is based on an in situ reaction and a straightforward transformation of Se nanowire template [7]. In our previous report of the synthesis of Bi$_2$O$_3$ nanotubes from Bi nanotubes [3] and Bi$_2$S$_3$ nanorods
from Bi nanotubes [26], we have provided a rational self-sacrificing template mechanism. For the transformation of MnOOH nanorods to LiMn$_2$O$_3$ nanorods, Yang et al. [12] and Zhang et al. [13] have also given the similar explanations. Herein, we hypothesize that the conversion of the manganese dioxide nanotubes and nanowires to lithium manganese oxide nanotubes and nanowires might be simply described by the schematic pictures in Figures 4(a) and 4(b). However, the intermediate process and the specific mechanism of the formation of the LiMn$_2$O$_3$ nanotubes and nanowires are not yet clear and warrant further investigation.

**4. Conclusions**

In conclusion, we have synthesized spinel phase LiMn$_2$O$_4$ nanotubes and nanowires via a low-temperature lithiation reaction, using $\beta$-MnO$_2$ nanotubes and $\alpha$-MnO$_2$ nanowires as the precursors. Besides, we hypothesize that the formation process of the as-prepared LiMn$_2$O$_4$ nanotubes and nanowires is based on a self-sacrificing template converting mechanism. This method requires no complex apparatus or technique, and the conditions are mild, and the present
study may supply a general strategy to design and synthesize nanostructured oxide materials.

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