Nanostructural evolution from nanosheets to one-dimensional nanoparticles for manganese oxide

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ABSTRACT

This paper introduces a novel hydrothermal soft chemical synthesis process for manganese oxide nanostructured particles using two-dimensional manganese oxide nanosheets as precursor. In this process, a birnessite-type manganese oxide with a layered structure was exfoliated into its elementary layer nanosheets, and then the nanosheets were hydrothermally treated to transform the two-dimensional morphology of the nanosheets to one-dimensional nanoparticles. The manganese oxide nanofibers, nanotubes, nanobelts, nanoribbons, and fabric-ribbon-like particles constructed from nanofibers or nanobelts were obtained using this hydrothermal soft chemical process. The nanostructural evolution from the two-dimensional nanosheets to the one-dimensional nanoparticles was characterized by XRD, SEM, TEM, and TG-DTA analysis. The morphology and nanostructure of the products are strongly dependent on the molecular dimension of organic amine cations added in the reaction system. The organic amine cations act as a morphology directing agent in the nanostructural evolution process.

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1. Introduction

Transition metal oxide nanomaterials attract much attention due to their unique electronic, optical, photonic, and catalytic properties [1,2]. The manganese oxides have been extensively studied as a well-known transition-metal oxide because the manganese oxides have outstanding structural multiformity and unique chemical and physical properties. The manganese oxides have potential applications in ion sieves [3,4], molecular sieves [5–7], catalysts [8,9], cathode materials of secondary rechargeable batteries [10,11], supercapacitors [12,13], and new magnetic materials [14,15]. The nanoscale manganese oxides are interesting in both applied and basic researches because of their excellent physical and chemical properties [16–18]. Up to now, some manganese oxide nanomaterials, such as nanorods, nanowires, nanotubes, and urchin-like nanostructure, have been reported [5,16,19–22]. Solution processes are useful for the manganese oxide nanomaterials synthesis. In the solution processes, usually oxidation reaction of Mn(II) salts or reduction reaction of Mn(VII) salts are used for the preparations of manganese oxide nanomaterials [20].

Exfoliation techniques for layered compounds are interesting and useful for the preparation of the nanomaterials [23]. The exfoliation of layered compounds into the constituent single layers provides a new class of two-dimensional nanoscale materials [24,25]. These unilamellar crystallites have a thickness on the order of nanometers or smaller, with lateral dimensions of submicro to micrometers. This extremely high anisotropy and the thickness of molecular dimensions are strikingly different from the nanoparticles with a generally spherical shape. Thus, the exfoliated nanosheets are useful nanomaterials with unique physicochemical properties. Other promising applications of the nanosheets are as precursors in the construction of nanostructured materials, such as preparations of multilayer thin film by layer-by-layer stacking of different kinds of nanosheets [26], sandwich layered compound by restacking two kinds of nanosheets [27], thin films by restacking the nanosheets on a substrate [28], and nanotubes by curling nanosheets [29].

The nanosheets are also a promising precursor in the nanoparticles synthesis because the nanosheets can be easily transformed to other nanoparticles by slightly changing their morphologies, which is greatly useful for the size- and shape-controlled synthesis of nanoparticles. We have prepared manganese oxide nanofibers by hydrothermal treatment of layered manganese oxide nanosheets [30] and ZnO nanoparticles by electron beam irradiation of Zn(OH)2-benzoate nanosheets [31]. We have also found that exfoliated layered titanate nanosheets can be transformed to TiO2 single

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nanocrystals under hydrothermal conditions, and the crystal morphology can be controlled by the reaction conditions [32–34]. The TiO$_2$ nanoparticles prepared by this method have specific crystal-plane on the surface, and show high performance as dye-sensitized solar cell electrode material [35].

In the present study, we describe nanostructural evolution of manganese oxide nanosheets under hydrothermal conditions and the morphology directing effect of organic amine cations in the nanostructural evolution process. A series of manganese oxide nanoparticles, including nanofibers, nanotubes, nanobelts, and nanoribbons, are formed in the nanostructural evolution process, and the nanostructures can be controlled using the organic amine cations as the morphology directing agent.

2. Experimental

2.1. Material preparation

A Na$^+$-form of birnessite-type manganese oxide (Na-Bir), which was used as a precursor for the preparation of manganese oxide nanosheets, was prepared by pouring a mixed solution of 3% H$_2$O$_2$ and 0.6 M NaOH (1000 mL) into a solution of 0.3 M Mn(NO$_3$)$_2$ (500 mL) under strong stirring conditions as described in literature [36]. The product was aged in the reaction solution at room temperature for one day. Then the product was filtered and washed with distilled water, and then dried at room temperature. An H$^+$-form of birnessite-type manganese oxide (H-Bir) was prepared from Na-Bir (10 g) by H$^+$/Na$^+$ ion-exchange reaction in a 1 M HNO$_3$ solution (1 L) for two times. Then H-Bir was dispersed in a 0.1 M tetramethylammonium hydroxide (TMAOH) solution with molar ratio of TMA/Mn = 5.5/2 under stirring conditions for two days, and then the sample was separated from the solution by centrifuge to obtain TMA$^+$-exchanged birnessite (TMA-Bir). An exfoliated birnessite nanosheet colloidal solution was obtained by dispersing TMA-Bir into distilled water under stirring conditions for 1 day [27,37]. The concentration of the TMA-Bir nanosheet solution was adjusted to 0.01 mol(Mn)/L with distilled water.

An OTA-Bir nanocomposite slurry solution was prepared by slowly dropping a 0.1 M n-octyltrimethylammonium chloride (OTA-Cl) solution (150 mL) into 500 mL of the TMA-Bir nanosheet solution under stirring conditions at room temperature with a molar ratio of OTA/Mn = 3/1. A BTA-Bir nanocomposite slurry solution was also prepared in a similar manner using a benzyltrimethylammonium chlorite (BTA-Cl) solution. The TMA-Bir nanosheet colloidal solution, OTA-Bir nanocomposite slurry solution, or BTA-Bir nanocomposite slurry solution (50 mL) was sealed in a Teflon-lined stainless steel vessel with an internal volume of 80 mL, which was then hydrothermally treated at a desired temperature for 24 h. After the hydrothermal treatment, the sample was separated from the solution by centrifuge, washed with distilled water, and finally dried using a freeze drier.

2.2. Physical analysis

The crystal structures of samples were investigated using a powder X-ray diffractometer (SHIMADZU XRD-6100) with Cu Kα (λ = 0.15418 nm) radiation. The particle size and morphology were characterized by scanning electron microscopy (SEM, JEOL JSM-5500S). Transmission electron microscopy (TEM) observation was performed on a JEOL JEM-3010 at 300 kV, where the nanoparticle sample was supported on a microgrid. Simultaneous thermo-gravimetry and differential thermal analysis (TG-DTA) were carried out on a SHIMADZU DTG-60H at a heating rate of 10 °C/min. For the measurement of BET surface area and pore size distribution of the samples, nitrogen gas adsorptions were carried out on a QUANTACHROME AUTOSORB-1-MP apparatus. Pore size

distribution and pore volume were evaluated using the Barrett–Joyner–Halenda (BJH) method.

3. Results and discussion

3.1. Hydrothermal reaction system of TMA-Bir nanosheets

A Na$^+$-form of birnessite-type manganese oxide (Na-Bir) with a layered structure is used as the precursor for the preparation of manganese oxide nanosheets. Na-Bir is treated in a HNO$_3$ solution to obtain an H$^+$-form of birnessite-type manganese oxide (H-Bir), and then H-Bir is treated in a tetramethylammonium hydroxide (TMAOH) solution to prepare the manganese oxide nanosheets. Fig. 1 presents XRD patterns of the layered manganese oxides samples dried at room temperature. H-Bir retains the layered structure of birnessite after the H$^+$/Na$^+$ ion-exchange reaction. TMA-Bir retains the layered structure also after the TMA$^+$/H$^+$ ion-exchange reaction in TMAOH solution, but the basal spacing increases from 0.73 to 0.96 nm. It has been reported that TMA-Bir has a basal spacing of 1.56 nm at wet state, and change its basal spacing to 0.96 nm after drying at room temperature [37]. The XRD result of Fig. 1 indicates that TMA$^+$ ions are intercalated into the interlayer space of the layered structure in TMA-Bir sample. When TMA-Bir is dispersed in distilled water, a colloidal solution is formed; suggesting that TMA-Bir is exfoliated into its nanosheets. H-Bir has platelike particle morphology with about 3 μm in width and 0.2 μm in thickness (Fig. 2(a)). Sheet-like particles with above 10 μm in width are formed after a drying-treatment of the TMA-Bir nanosheet colloidal solution (Fig. 2(b)). This result reveals that the exfoliated TMA-Bir nanosheets restack to TMA-Bir with sheet-like particle morphology after the drying-treatment.

Fig. 3 presents the XRD patterns of samples obtained by hydrothermal treatment of the TMA-Bir nanosheet colloidal solution. TMA-Bir retains the layered structure up to 130 °C, but the basal spacing decreases from 0.96 to 0.75 nm and the crystallinity decreases also with increasing the hydrothermal reaction temperature. A TG-DTA analysis reveals that the decrease of the basal spacing accompanies release of interlayer TMA$^+$ ions from the layered phase into the solution (see Fig. S1). The particle morphology change in the hydrothermal reaction process is investigated using SEM and TEM as shown in Fig. 2. The sheet-like particles of TMA-Bir change to nanoribbon-like particles in a temperature range of 100–120 °C (Fig. 2(c)), and fabric-ribbon-like particles constructed from nanofibers are formed at 130 °C (Fig. 2(d)), although they retain the layered structure. The TEM nanostructural study indicates that TMA-Bir is exfoliated into the manganese oxide nanosheets after the exfoliation treatment
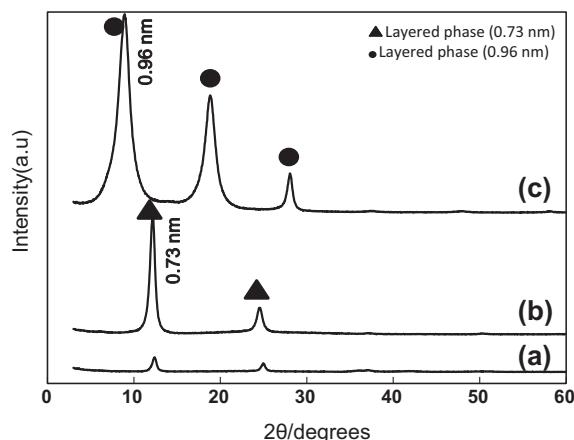

Fig. 1. XRD patterns of (a) Na-Bir, (b) H-Bir, and (c) TMA-Bir.