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Synthesis, characterization and magnetic properties of β-MnO_2 nanorods

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Abstract

β-MnO_2 nanorods were successfully prepared by a simple refluxing route using manganese sulfate ($MnSO_4 \cdot H_2O$), sodium persulfate ($Na_2S_2O_8$) and sodium hydroxide (NaOH) as the raw materials. The product was characterized by XRD, SEM, TEM, ED, EDX and TG-DTG. The results showed that the nanostructured materials were exactly manganese dioxides (pyrolusite) with rutile crystal structures and the diameter of β-MnO_2 nanorods ranged from 50 to 80 nm and the length ranged from 1.0 to 2.0 μm. Meanwhile, the high yield (~70%) of high-quality β-MnO_2 nanorods can be attained. The magnetic properties of the products have been evaluated using a vibrating magnetometer, which showed that the β-MnO_2 nanorods exhibited ferromagnetic characteristics at room temperature.

Keywords: Manganese dioxide; Nanorods; Formation mechanism; Ferromagnetic characteristics

1. Introduction

MnO_2, an important substance used widely as cathodic materials, catalysts or magnetic materials [1], is a non-stoichiometric compound and has many crystalline forms such as α-, β-, γ- and δ-type, etc [2]. Great attention has been paid to synthesis of manganese dioxides with different crystallographic structure. On the basis of the redox reactions of MnO_4^- and/or Mn^{2+}, several methods have been evolved in the preparation of manganese dioxides with controlled morphologies and crystalline structures. These methods include thermal [3], refluxing [4–6], hydrothermal [7], sol-gel [8,9], electrochemical [10], as well as solid-state reaction [11]. The influences of pH, counteractions, temperature, concentrations, and anions on the crystallinity and crystal forms of the final products have been extensively studied. In most of the previous reported synthetic routes, the formation of different tunnel structures have been controlled through the adjustment of the pH with H_2SO_4 or NaOH solution [5], for example, α- and λ-MnO_2 tend to be favored in aqueous concentrated acid [4–6], whereas δ-MnO_2 forms preferentially in aqueous concentrated base [12]. Luo and Suib [12] have found that increasing the basicity of the system is beneficial for the increase of the crystallization rate and the high yield of δ-MnO_2 layer structures.

Recently, much effort has been made to preparation of low-dimensional nanostructured MnO_2 because dimensionality is a crucial factor in determining the properties of nanomaterials. For example, Li and co-workers [13,14] reported the hydrothermal preparation of α-MnO_2 nanowires by oxidizing $MnSO_4$ in $KMnO_4$ and $(NH_4)_2S_2O_8$, respectively. They concluded that the cation concentrations were vital to the formation of these tunnel structures. It was reported that γ-MnO_2 nanowires can be synthesized through a coordination-polymer-precursor route [15]. Also, γ-MnO_2 nanowires can be prepared by facile hydrothermal treatment of commercial granular γ-MnO_2 crystals [16]. Al-Sagheer and Zaki [17] reported the preparation of pure δ-MnO_2 nanorods by sol-gel method. α-, γ- and δ-MnO_2 contain significant amounts of small molecules or ions as integral parts of the structure, while β-MnO_2 (pyrolusite) is relatively pure MnO_2 with a rutile crystal structure [18]. β-MnO_2 nanorods have been prepared generally under strict conditions. Wang and Li [14] reported the hydrothermal

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preparation of β-MnO_2 nanorods by strictly controlling the cation concentrations. The yield of β-MnO_2 nanorods from this method is very low. Xi and co-workers [19] reported the synthesis of β-MnO_2 nanorods with high aspect ratios by calcinating λ-MnOOH nanorods precursor but very strict synthetic conditions are required for production of high-quality β-MnO_2 nanorods. It is thus of significance to design a facile route to synthesize high-quality β-MnO_2 nanorods with a high yield. Although much work has been done on nanostructured β-MnO_2 as cathodic and catalytic materials, there are few studies on nanostructured β-MnO_2 as magnetic materials. Furthermore, there is no report on the β-MnO_2 nanorods prepared by the refluxing route in the literature.

In this work, a simple refluxing route was reported for preparing β-MnO_2 nanorods without any physical template and surfactant. This method is quite simple and facile, without any catalyst or any template to direct the growth of nanorods. The structure and morphology of the products were characterized by XRD, SEM, TEM, ED, EDX and TG-DTG. Magnetic properties of such morphologically designed MnO_2 structure were examined by VSM.

2. Experiment

All the reagents were of analytical grade and used as received without further purification. Manganese sulfate ($MnSO_4{\cdot}H_2O$), sodium persulfate ($Na_2S_2O_8$) and sodium hydroxide (NaOH) were purchased from Beijing Chemical Reagent Co. (China). A typical synthesis was as follows: $MnSO_4{\cdot}H_2O$ (2 g) and $Na_2S_2O_8$ (2.82 g) were placed in deionized water at room temperature to form a homogeneous solution completely. A certain volume of NaOH aqueous solution (the molar fraction of OH^-/Mn^{2+} was 2) was added to the above solution. The pink solution changed to brown and was stirred at room temperature for 30 min until a suspending liquid was formed. All experimental processes were under magnetic stirring. First, the suspending liquid was refluxed at 50 °C for 18 h, then refluxed at 80 °C for 5 h, finally at 100 °C for 3 h. After the reaction was complete, the resulting brownish-black solid product was filtered off, then rinsed with deionized water and absolute ethyl alcohol several times to remove ions possibly remaining in the final product, and finally dried at 80 °C in air. According to the practical and theoretical weight, the product yield can be calculated.

The products were characterized by X-ray power diffraction (XRD) using a M18XCE X-ray power diffractometer equipped with graphite-monochromated Cu-Kα radiation ($\lambda = 1.54178$ Å), employing a scanning rate of 0.02° s^{-1} in the 2θ ranging from 10° to 70°. The TEM photographs and the electron diffraction (ED) pattern were recorded on a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. The scanning electron microscopy (SEM) images and EDX were obtained using a HITACHI S-4300 microscope and EMAX Horiba, respectively. Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis was performed on a NETZSCH STA 409 PC instrument in flowing air with a temperature-increasing rate of 10 °C/min. Their magnetic properties at room temperature were investigated using a vibrating sample magnetometer (VSM, Lakeshore 7307, USA).

3. Results and discussion

Wang et al. had proposed a wet chemical method using manganese sulfate and sodium persulfate to get the high pure battery-grade γ-MnO_2 [20]. We extended this method here for preparation of β-MnO_2 nanorods. First, the Mn^{2+} reacted with NaOH to produce amorphous $Mn(OH)_2$ at room temperature, and then the mixed system was stirred and heated according to temperature rise procedure, which led to the formation of MnO_2 with regular shapes. The whole reaction can be represented as follows:

$$MnSO_4 + Na_2S_2O_8 + 4NaOH \rightarrow MnO_2 + 3Na_2SO_4 + 2H_2O \quad (1)$$

It was reported that one-dimensional nanostructures can be obtained from the rolling of a natural or artificial lamellar structure [21]. Under certain conditions, a layer structure would begin to curl, and the thus-obtained tubular structure could serve as the original driving force for the growth of one-dimensional nanostructures. Among the several crystallographic forms of MnO_2, δ-MnO_2 alone has a layer structure, which is indispensable in the formation of β-MnO_2 nanorods. A schematic representation of the steps involved in the synthesis of β-MnO_2

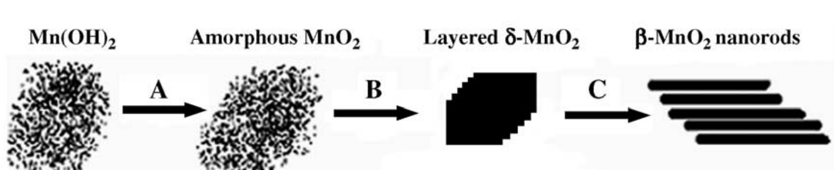

Fig. 1. Schematic representation of the synthesis process of β-MnO_2 nanorods.