

Preparation of Mn_3O_4 nanocrystallites by low-temperature solvothermal treatment of γ - $MnOOH$ nanowires

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Abstract

The preparation of trimanganese tetroxide (Mn_3O_4) nanocrystallites from γ - $MnOOH$ nanowires under mild conditions has been achieved by two steps: first, γ - $MnOOH$ nanowires with a mean diameter of about 12 nm and lengths of up to several micrometers were directly prepared via hydrothermal reaction between $KMnO_4$ and toluene in water at 180°C for 24 h; then, pure Mn_3O_4 nanocrystallites could be obtained by solvothermal treatment of the γ - $MnOOH$ nanowires in ethylenediamine (EDA) and ethylene glycol (EG) at 150°C for 24 h. It was found that the Mn_3O_4 product obtained in EDA comprised well-defined nanocrystallites with the size in the range of 15–35 nm, while the one obtained in EG consisted of aggregated nanoparticles with the size of less than 18 nm. The possible formation mechanism of nanocrystalline Mn_3O_4 in EDA and EG and reasons for the different effects of various solvents on the products were also proposed.

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1. Introduction

The powder of trimanganese tetroxide (Mn_3O_4) is known to be an active catalyst for the oxidation of methane and carbon monoxide [1], the selective reduction of nitrobenzene [2], or the combustion of organic compounds at temperatures of 373–773 K which is of interest in alleviating several air-pollution problems [3,4]. It has also been used as a starting material in the preparation of Li–Mn–O electrode materials for rechargeable lithium batteries [5,6] and soft magnetic materials such as manganese zinc ferrite which is useful for magnetic cores in transformers for power supplies [7]. Nanometer-sized Mn_3O_4 powders with remarkably increased surface area are expected to display better performance in all the above-mentioned aspects of applications. For instance, a much larger surface-to-volume ratio can surely improve the catalysis capacity of Mn_3O_4 powders due to more adsorption of oxygen

for the oxidation of carbon monoxide and nitrogen oxides [1,8,9].

Mn_3O_4 powders were usually prepared by heating either manganese oxides with a higher valence of manganese (e.g., MnO_2 , Mn_5O_8 , and Mn_2O_3 , etc.) or Mn(II) and Mn(III) hydroxide, oxyhydroxide, carbonate, nitrate, and sulfate at about 1000°C in air [10–12]. However, these calcining methods were apt to yield products with a form of hard solid or coarse grains. Another conventional process to synthesize Mn_3O_4 powders was sol-gel technique, which still need post-treatment at high temperatures [13,14]. Currently, there is obviously a trend toward devising simple, low-temperature solution chemical synthetic methods for nanomaterials preparation. Hydrothermal/solvothermal technique is among the most promising solution chemical routes to synthesize nanocrystallites generally below 250°C [15,16]. The distinct advantage of such a soft solution process is to induce the preparation of high-crystallized powders with narrow grain size distribution and high purity without post-treatment at high temperatures [17]. In addition, the particle properties such as morphology and size can be well controlled

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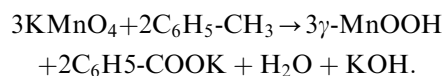
during the hydrothermal/solvothermal process. Recently, a low-temperature solvothermal method to Mn_3O_4 nanoparticles has been successfully developed, which was based on the reaction of KMnO_4 and a great excess of CH_3OH or $\text{CH}_3\text{CH}_2\text{OH}$ (CH_3OH or $\text{CH}_3\text{CH}_2\text{OH}$ served as both the reducing agent and the solvent) at 80–170°C [18]. However, the strong oxidation capability of KMnO_4 and large volume of flammable and toxic CH_3OH or $\text{CH}_3\text{CH}_2\text{OH}$ used in this solvothermal route made it somewhat dangerous.

In this work, we report a facile novel solvothermal way to prepare Mn_3O_4 nanocrystallites from $\gamma\text{-MnOOH}$ nanowires under mild conditions. First, $\gamma\text{-MnOOH}$ nanowires with an average diameter of about 12 nm and lengths of up to several micrometers, which were used here as the special precursor to Mn_3O_4 nanocrystallites, were directly prepared through hydrothermal reaction between KMnO_4 and toluene in water at 180°C for 24 h. Then, subsequent solvothermal treatment of the as-prepared $\gamma\text{-MnOOH}$ nanowires in ethylenediamine (EDA) and ethylene glycol (EG) at 150°C for 24 h would produce phase-pure Mn_3O_4 nanocrystallites, which have been characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectrum (FTIR) and wet chemical analysis, and transmission electron microscopy (TEM). The possible formation mechanism of nanocrystalline Mn_3O_4 in EDA and EG and reasons for the different effects of solvents on the products were also discussed.

2. Experimental

2.1. Preparation of $\gamma\text{-MnOOH}$ nanowires and Mn_3O_4 nanocrystallites

All the reagents used in the experiments were of analytically pure grade without any further purification. $\gamma\text{-MnOOH}$ nanowires were prepared via the hydrothermal reaction between KMnO_4 and toluene in water at 180°C for 24 h, according to the following equation:



In a typical procedure for the preparation of Mn_3O_4 nanocrystallites, 0.5 g of the as-prepared $\gamma\text{-MnOOH}$ nanowires was put into a Teflon-lined stainless-steel autoclave of 50 mL capacity, to which 40 mL of EDA or EG was added. The autoclave was sealed and maintained at 150°C for 24 h, then it was allowed to cool to room temperature naturally. The as-formed precipitate was filtered, washed with deionized water and ethanol for several times, and dried at room temperature in the air.

2.2. Characterization of the as-prepared precursor and product

Powder XRD patterns of the as-prepared precursor and products were measured at a scanning rate of 8°min^{-1} in the 2θ range from 10 to 70° , using a Japan Mac Science M03XHF²² X-ray diffractometer ($\text{CuK}\alpha$ radiation, $\lambda = 1.54056 \text{ \AA}$; 40 KV; 40 mA). The TEM images of the as-prepared precursor and products were taken with a Philips Tecnai12 TEM at an accelerating voltage of 120.0 KV. FTIR of the obtained products in the wave number range of 1600–400 cm^{-1} were recorded on a Nicolet AVARAT360 FT-IR Spectrometer at room temperature with samples in a KBr wafer. The manganese content in the obtained products was determined with the proposed EDTA titrimetric method [19].

3. Results and discussions

Fig. 1 shows the XRD patterns of the as-prepared precursor. All its diffraction peaks could be assigned to $\gamma\text{-MnOOH}$. The lattice parameters obtained by refinement of the XRD data were $a = 8.1577 \text{ \AA}$, $b = 5.1776 \text{ \AA}$, and $c = 5.2278 \text{ \AA}$, which also agreed with those of $\gamma\text{-MnOOH}$ reported in the JCPDS Card (File No. 41-1379). The extremely narrow and strong diffraction peak positioned at $2\theta = 26.2^\circ$ may suggest the preferential growth of $\gamma\text{-MnOOH}$ under the hydrothermal condition. From the TEM image of the as-prepared precursor shown in Fig. 2, it can be seen that bulk quantity of $\gamma\text{-MnOOH}$ nanowires with a relatively uniform diameter of about 12 nm and length of up to several micrometers were synthesized directly from the hydrothermal reaction between KMnO_4 and toluene in water at 180°C, without the addition of any surfactant as the structure-directing template. It is well accepted

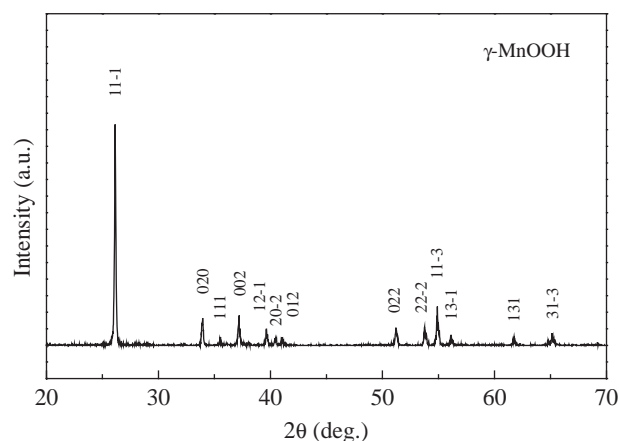


Fig. 1. XRD pattern of the as-prepared precursor.

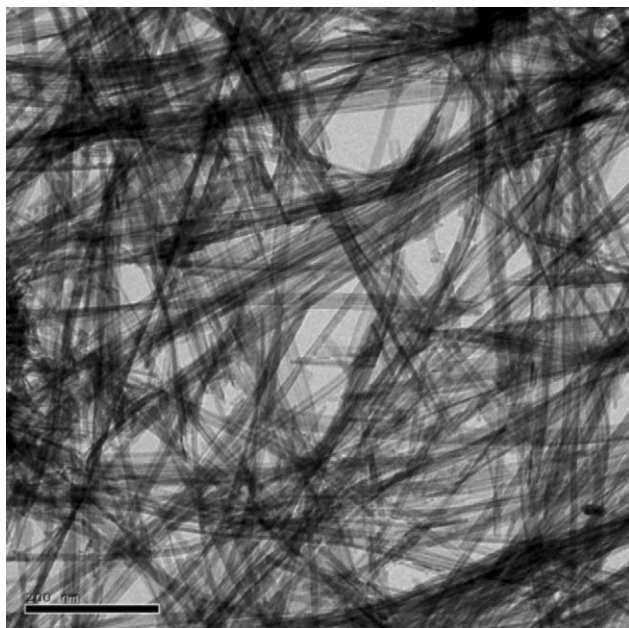


Fig. 2. TEM image of the as-prepared precursor.

that utilization of nanoscaled powders as the starting material can lead to milder preparation conditions for a target product [20,21]. However, the previously reported hydrothermal methods to MnOOH powders with elongated morphologies always need the assistance of surfactants to direct the crystallization of the reactants in the desired products [22,23]. The easy preparation of γ -MnOOH nanowires in our study makes it more practicable to be used as a precursor to nanocrystalline Mn_3O_4 .

Fig. 3 shows the XRD patterns of the obtained products via solvothermal treatment of the γ -MnOOH nanowires in EDA (Fig. 3a) and EG (Fig. 3b) at 150°C for 24 h. As could be seen from Fig. 3, both products displayed the similar XRD patterns corresponding to the tetragonal cell of Mn_3O_4 (Hausmannite). The lattice parameters obtained by refinement of the XRD data were $a = 5.7589$ and $c = 9.4662 \text{ \AA}$ for the Mn_3O_4 synthesized in EDA and $a = 5.7641$ and $c = 9.4482 \text{ \AA}$ for that in EG, which were also consistent with those of Mn_3O_4 reported in the JCPDF card (File No. 27-734). However, the diffraction peaks of the Mn_3O_4 powders obtained in EG were obviously wider and weaker than those of the Mn_3O_4 powders obtained in EDA, suggesting that the Mn_3O_4 powders obtained in EDA were larger and better crystallized than those obtained in EG according to the Debye–Scherrer formula [24].

Fig. 4 shows the FTIR spectra of the obtained Mn_3O_4 powders by solvothermal treatment of the γ -MnOOH nanowires in EDA (Fig. 4a) and EG (Fig. 4b) at 150°C for 24 h. It can be seen from Fig. 4 that there were no characteristic IR absorption bands of EDA and EG, indicating that both of the Mn_3O_4 products were free of

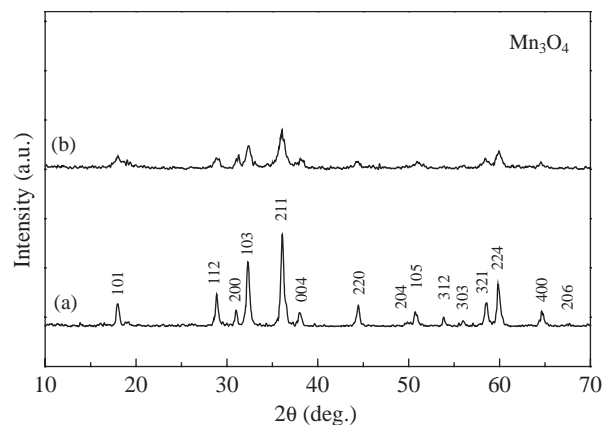


Fig. 3. XRD patterns of the obtained products via solvothermal treatment of the γ -MnOOH nanowires in EDA (a) and EG (b) at 150°C for 24 h.

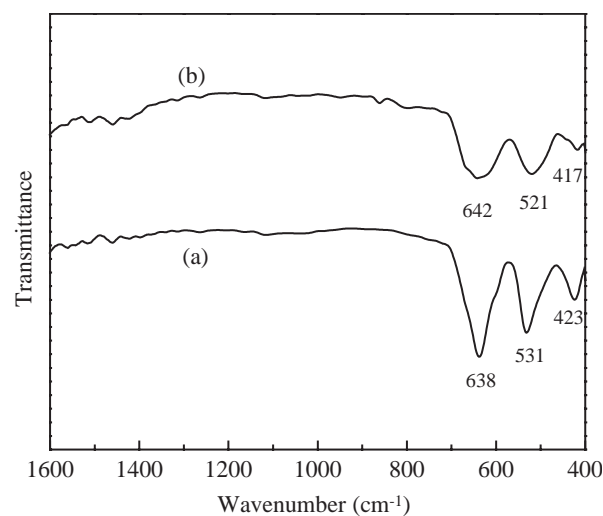


Fig. 4. FTIR spectra of the obtained Mn_3O_4 powders via solvothermal treatment of the γ -MnOOH nanowires in EDA (a) and EG (b) at 150°C for 24 h.

the solvents. The FTIR spectra of both products demonstrated a notable resemblance to those of Mn_3O_4 in the previous studies [25–27]. In the region from 650 to 500 cm^{-1} , two absorption peaks were observed at 638 and 531 cm^{-1} for the Mn_3O_4 obtained in EDA or at 642 and 521 cm^{-1} for that obtained in EG. These absorption peaks may be associated with the coupling modes between the Mn–O stretching modes of tetrahedral and octahedral sites [27]. In the region from 500 to 400 cm^{-1} , the absorption peaks at 423 and 417 cm^{-1} were observed for the Mn_3O_4 obtained in EDA and EG, respectively. These absorption peaks were attributed to the band stretching modes of the octahedral sites; displacement of the Mn^{2+} ions in the tetrahedral sites was negligible [27]. Moreover, the manganese contents in both products determined by the proposed EDTA titrimetric method [19] were close

to 72.0% (m m^{-1}), which corresponds to the theoretical value of manganese content in Mn_3O_4 . Thus, the FTIR spectra and wet chemical analysis further confirmed that the obtained products in both solvents were composed of Mn_3O_4 .

Fig. 5 shows the TEM images of the obtained Mn_3O_4 powders by solvothermal treatment of the $\gamma\text{-MnOOH}$ nanowires in EDA (Fig. 5a) and EG (Fig. 5b) at 150°C for 24 h. It was clear from Fig. 5a that the obtained Mn_3O_4 in EDA was composed of well-defined nanocrystallites with the size ranging from 15 to 35 nm. On

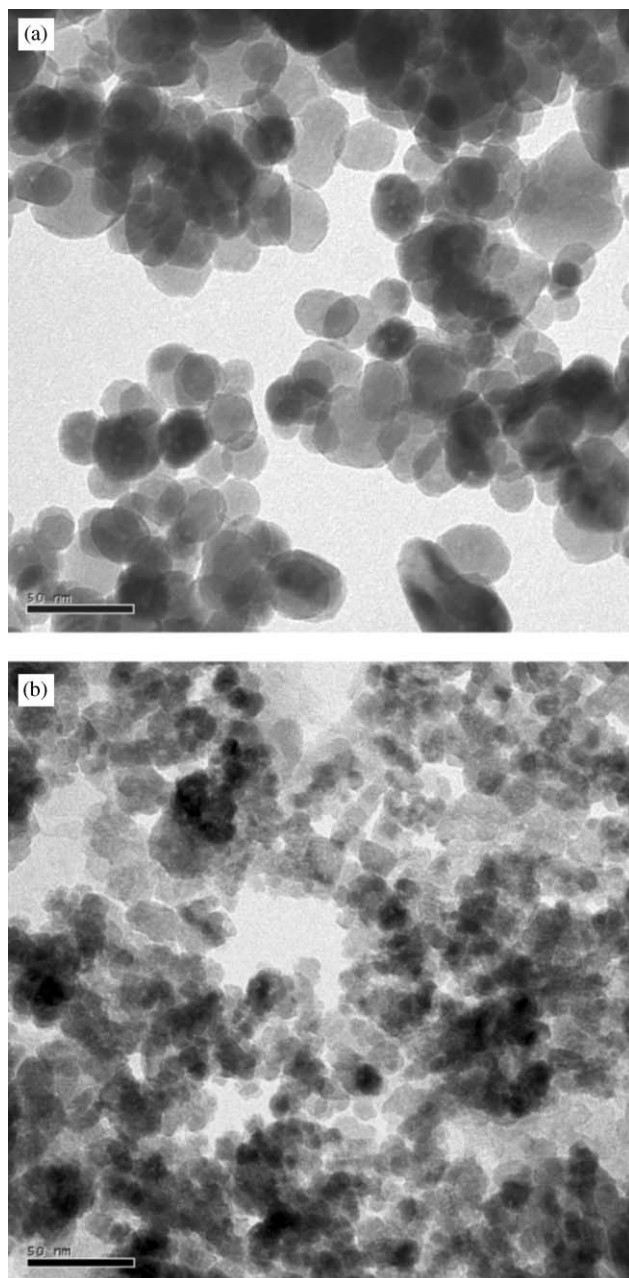


Fig. 5. TEM images of the obtained Mn_3O_4 powders via solvothermal treatment of the $\gamma\text{-MnOOH}$ nanowires in EDA (a) and EG (b) at 150°C for 24 h.

the other hand, the obtained Mn_3O_4 in EG as shown in Fig. 5b consisted of aggregated nanoparticles whose sizes were less than 18 nm, together with a certain amount of amorphous substance. The TEM images of the obtained Mn_3O_4 powders in two solvents were in accordance with their XRD patterns shown in Fig. 3.

For the solvothermal treatment processes, EDA and EG were selected as the solvents chiefly due to their moderate reducibility [28–31]. In the high-pressure and alkalescent system, EDA mainly takes the role of electron transfer, displaying moderate intensity reductive characteristic [28,29]. For example, single crystalline metallic bismuth nanowires have been successfully prepared by a low-temperature (160°C) solvothermal method through the reduction of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ by EDA, which acts as a solvent as well [29]. In like manner, as a moderate reducing agent, EG has been widely employed in the reduction of a suitable inorganic/organic metal salt under solvothermal conditions for producing nanostructured metal powders [31,32]. Therefore, it is suggested that in our case, the formation of Mn_3O_4 nanocrystallites by solvothermal treatment of $\gamma\text{-MnOOH}$ nanowires in pure EDA and EG at 150°C may also be from a typical solvothermal reduction process. Being strongly polarizing and chelating solvents, EDA and EG can greatly enhance solubility, diffusion, and reactivity of the reactant species. Especially, when EDA and EG coordinated with Mn^{3+} , the short distance between manganese and nitrogen or oxygen atom in the coordination compound is favorable for electron to transfer from N or O to Mn^{3+} [29,30], resulting in the reduction of $\gamma\text{-MnOOH}$ to Mn_3O_4 . Meanwhile, the elevated pressure autogenerated in the solvothermal system affords a greater driving force for the reaction process [32,33]. To improve our understanding of the solvothermal reduction mechanism, experiments were performed under similar conditions when EDA and EG were replaced by several non-reducibility (or less reducibility) solvents such as tetrachloride, *n*-hexane, benzene, pyridine, acetone, and dimethylsulfoxide. The analysis results demonstrated that in these non-reducibility (or less reducibility) solvents, the solid-state phase was still $\gamma\text{-MnOOH}$, indicating the solvothermal reduction reactions were not initiated. Owing to the different chemical and physical properties of EDA and EG, such as basicity, chelation, vapor pressure, and viscosity, etc. [34], they exerted a diverse influence on the formation of Mn_3O_4 . The chances are that the stronger basicity and chelation, less tendency to form dimer and trimer at high temperature, higher vapor pressure, and lower viscosity of EDA favor the solubility, diffusion, reaction of the reactant species, or the subsequent crystal growth of Mn_3O_4 . Consequently, when the reaction temperature and reaction time were kept constant (e.g., 150°C, 24 h),

the solvothermally derived Mn_3O_4 in EDA would grow larger with higher crystallinity than the one in EG. However, the detailed reaction mechanism between Mn_3O_4 and EDA or EG under solvothermal conditions is still under investigation.

4. Conclusions

In summary, γ - MnOOH nanowires with an average diameter of about 12 nm and lengths of up to several micrometers were directly prepared through hydrothermal reaction between KMnO_4 and toluene in water at 180°C for 24 h, and phase-pure Mn_3O_4 nanocrystallites were successfully synthesized by solvothermal treatment of the γ - MnOOH nanowires in EDA and EG at a relatively low temperature of 150°C for 24 h, which have been characterized using XRD, FTIR, TEM, and wet chemical analysis. The as-synthesized Mn_3O_4 in EDA comprised well-defined nanocrystallites with the size in the range of 15–35 nm, while the one obtained in EG consisted of aggregated nanoparticles with the size of less than 18 nm. It was suggested that the formation of Mn_3O_4 nanocrystallites in EDA and EG be derived from a typical solvothermal reduction process. The possible reasons for the different effects of solvents on the products were also discussed. The proposed low-temperature solvothermal methods to γ - MnOOH nanowires and Mn_3O_4 nanocrystallites in the present work were simple, safe, and low cost, which made it very suitable to be scaled up for industrial production.

Acknowledgments

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