

Nanorods of manganese oxides: Synthesis, characterization and catalytic application

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Abstract

Single-crystalline nanorods of β -MnO₂, α -Mn₂O₃ and Mn₃O₄ were successfully synthesized via the heat-treatment of γ -MnOOH nanorods, which were prepared through a hydrothermal method in advance. The calcination process of γ -MnOOH nanorods was studied with the help of Thermogravimetric analysis and X-ray powder diffraction. When the calcinations were conducted in air from 250 to 1050 °C, the precursor γ -MnOOH was first changed to β -MnO₂, then to α -Mn₂O₃ and finally to Mn₃O₄. When calcined in N₂ atmosphere, γ -MnOOH was directly converted into Mn₃O₄ at as low as 500 °C. Transmission electron microscopy (TEM) and high-resolution TEM were also used to characterize the products. The obtained manganese oxides maintain the one-dimensional morphology similar to the precursor γ -MnOOH nanorods. Further experiments show that the as-prepared manganese oxide nanorods have catalytic effect on the oxidation and decomposition of the methylene blue (MB) dye with H₂O₂.

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1. Introduction

Manganese oxides with a rather complex oxide system, forming several phases such as MnO, MnO₂, Mn₂O₃ and Mn₃O₄, are of considerable importance in many technological applications. Mn₂O₃ is known to be an active catalyst for removing carbon monoxide and nitrogen oxide from waste gas [1,2], MnO₂ and Mn₃O₄ for the oxidation of methane and carbon monoxide or the selective reduction of nitrobenzene [3–5]. Mn₂O₃ and Mn₃O₄ have also been used to produce soft magnetic materials, such as manganese zinc ferrite [6,7]. And in the last decade, considerable attention has been focused on lithiation of Mn-oxides for intercalation compounds of Li–Mn–O as electrode materials for rechargeable lithium batteries [8–12].

Recently, the synthesis of one-dimensional (1D) nanostructures has attracted considerable attention because 1D nanostructures have potential applications in wide-ranging sectors including catalysis, sensing, electronics and photo-electronics, with performances that are anticipated to be superior to those of their bulk counterparts [13,14]. For example, 1D nanostructured MnO₂ may provide the possibility of detecting the theoretical operating limits of a lithium battery as the 1D systems are the smallest dimension structures for efficient transport of electrons [15,16], and may give an ideal host material for the insertion and extraction of lithium ions. Suib et al. found that the catalytic performance of nanoribbon-like Mg-todorokite materials in converting benzyl alcohol to benzaldehyde was improved greatly compared to that of the bulk Mg-todorokite [17].

Many efforts are being made to prepare 1D nanostructured crystalline manganese oxides and several groups have reported the synthesis of 1D nanostructured manganese

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oxides. Xie Yi et al. have obtained γ -MnO₂ nanowires by a hydrothermal chemical reaction of a coordination polymer [$\{\text{Mn}(\text{SO}_4)(4,4\text{-bpy})(\text{H}_2\text{O})_2\}_n$] in NaOH solution [18]. Li Yadong has reported a hydrothermal method to synthesize single-crystalline α -MnO₂ nanowires and β -MnO₂ nanorods [19]. Yuan Zhongyuan et al. have synthesized single-crystalline α -Mn₂O₃ nanorods by ammonia-hydrothermal treatment of commercial granular/bulky MnO₂ [20]. Shao Changlu et al. used an electrospinning technique to get α -Mn₂O₃ and Mn₃O₄ nanofibers, which involves several steps such as preparation of a gel, electrospinning and calcination [21]. Wang Wenzhong et al. have synthesized Mn₃O₄ nanowires at 850 °C in NaCl flux through heat treatment of nanosized MnCO₃ precursors [22]. In last 2 years, several groups have reported the preparation of β -MnO₂ nanorods/nanowires and/or Mn₃O₄ nanorods/nanoparticles through a γ -MnOOH precursor route [23–27]. However, few systematic preparations of 1D nanostructured manganese oxides were reported.

In this paper, we report a systematic synthesis of manganese oxide nanorods via the heat-treatment of γ -MnOOH nanorod precursors, which were prepared through a hydrothermal method in advance. β -MnO₂, α -Mn₂O₃ and Mn₃O₄ nanorods with morphology similar to the precursors' are successfully obtained, respectively, through the heat-treatment of γ -MnOOH nanorods at different temperatures in air. Another important aspect of this work is the successful preparation of the Mn₃O₄ nanorods via the heat-treatment of γ -MnOOH nanorods under flowing N₂ atmosphere at much lower temperatures than in air. This innovation not only saves much energy but also is helpful for Mn₃O₄ sample to retain the nanorod morphology similar to the precursors'. Our approach requires neither complex apparatus nor sophisticated techniques. The successful synthesis of the γ -MnOOH nanorod precursor in a large-sized autoclave (1 L) via hydrothermal reactions has provided the advantage for the large-scale preparation of 1D nanostructured manganese oxides, which is essential for application study. Further experiments reveal that the as-prepared manganese oxide nanorods show catalytic efficiency in the oxidation and decomposition of the methylene blue (MB) dye with H₂O₂.

2. Experimental section

2.1. Preparation of nanostructured precursor γ -MnOOH

The reagents KMnO₄ and CH₃CH₂OH are analytical grade from Shanghai Chemicals Company and were used without further purification. The preparation of the precursor γ -MnOOH nanorods was similar to our previous report [28]. In a typical procedure, 4 g of KMnO₄, 4 mL of CH₃CH₂OH and 400 mL of distilled water were put in a stainless steel autoclave of 1 L capacity with a magnetic stirrer and then the autoclave was sealed and kept at 100–150 °C for 24 h with a stirring rate of about 200 r/min, then it was allowed to cool to room temperature naturally. The product was collected after washing, filtering and drying in vacuum.

2.2. Preparation of manganese oxides

The as-prepared γ -MnOOH precursor was subsequently calcined in the temperature range of 250–1050 °C in a furnace for 4–16 h to get manganese oxides: β -MnO₂, α -Mn₂O₃ and Mn₃O₄ (see Table 1). In parallel, Mn₃O₄ was also prepared through calcining γ -MnOOH precursor under flowing N₂ atmosphere at 500–800 °C for 4–16 h.

2.3. Physical analysis

Thermogravimetric analysis (TGA) was carried on a Shimadzu TGA-50H thermogravimeter analyzer to determine the thermal behavior of the γ -MnOOH precursors. The experiments were conducted under an air atmosphere (20 mL/min) at a heating rate of 10 °C/min. X-ray powder diffraction (XRD) patterns were recorded on a Japan Rigaku D/max- γ B X-ray diffractometer with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$), operated at 40 kV and 80 mA. Transmission electron microscopy (TEM) images and electron diffraction (ED) images were taken with a Hitachi H-800 transmission electron microscope, performed at an accelerating voltage of 200 kV. The high-resolution TEM (HRTEM) observation was performed with a 200 kV electron microscope on JEOL-2010.

Table 1
Reaction conditions and corresponding products

Reaction temperature (°C)	Reaction time (h)	Reaction atmosphere	Composition of the products (XRD result)
250	3	Air	β -MnO ₂ + MnOOH
250–400	4–16	Air	β -MnO ₂
550	4–8	Air	β -MnO ₂ (main) + α -Mn ₂ O ₃ (minor)
550	8–16	Air	α -Mn ₂ O ₃ (main) + β -MnO ₂ (minor)
600–800	8–16	Air	α -Mn ₂ O ₃
850–950	8–16	Air	α -Mn ₂ O ₃ + Mn ₃ O ₄
1000–1050	8–16	Air	Mn ₃ O ₄
400	4–8	N ₂	MnOOH (main) + Mn ₃ O ₄ (minor)
400	8–16	N ₂	Mn ₃ O ₄ (main) + MnOOH (minor)
500–800	4–16	N ₂	Mn ₃ O ₄

2.4. Catalytic measurements

The obtained manganese oxides were used as catalysts for the oxidation and decoloration of the MB dye with H_2O_2 . The catalysts to be tested were dried at 110°C overnight beforehand to remove moisture. The MB and H_2O_2 are of analytical purity from Shanghai Chemicals Company and were used as received without further purification. The catalytic reaction was carried out in a 500 mL glass flask, which contained 62.5 mL of MB dye solution (125 mg/L), 162.5 mL of distilled water, and 125 mg of manganese oxides catalysts. After adding 25 mL of 30% (weight percent) H_2O_2 solution, the flask was sealed and the mixture was allowed to react at room temperature with continuous magnetic stirring. For a given time interval, 1 mL of the mixture solution was pipetted into a volumetric flask and quickly diluted with distilled water to 25 mL prior to analysis. For optical absorption measurements, the diluted solution was immediately centrifuged in order to remove the catalyst particles, which tend to scatter the incident beam. The centrifuged solution was then put into a quartz cell (path length 1.0 cm) and the absorption spectrum was measured with a Shimadzu UV-2550 ultraviolet-visible (UV-Vis) spectrophotometer. A linear calibration curve for the dye concentrations was obtained by monitoring the peak intensity at $\lambda_{\text{max}} = 664\text{ nm}$ for a series of standard solutions according to the Beer's law.

3. Results and discussion

First of all, TGA was carried out to investigate the thermal behavior of the $\gamma\text{-MnOOH}$ nanorods in air so as to guide the calcination procedure for the preparation of the target products. As can be seen in Fig. 1, three distinct peaks appear at 282.9, 558.2 and 891.8 $^\circ\text{C}$ in the DTGA curve, which is the first derivative of the TGA curve with three corresponding weight-loss steps. The first weight loss starts at about 200°C , showing a weight loss of 1.737%.

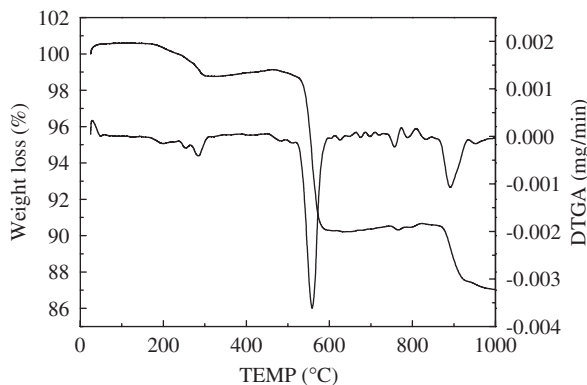


Fig. 1. Thermogravimetric analysis curves of the $\gamma\text{-MnOOH}$ precursor in air.

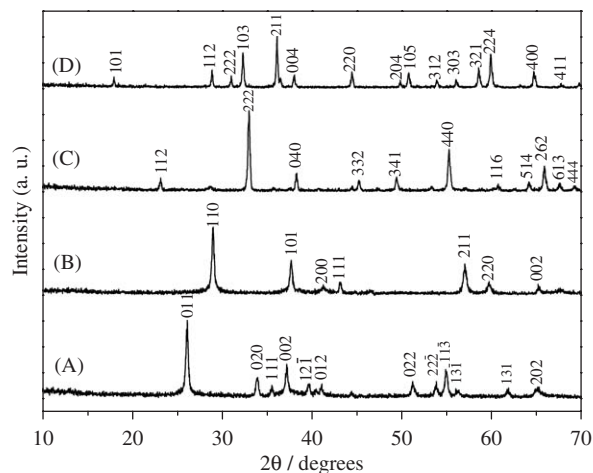


Fig. 2. The XRD patterns of the samples: (A) the precursor $\gamma\text{-MnOOH}$ nanorods; (B) the sample obtained through calcining the $\gamma\text{-MnOOH}$ precursor at 350°C for 4 h in air; (C) the sample obtained through calcining the $\gamma\text{-MnOOH}$ precursor at 600°C for 12 h in air; (D) the sample obtained through calcining the $\gamma\text{-MnOOH}$ precursor at 600°C for 8 h in the N_2 flux.

The second weight change starts at about 460°C with a weight loss of 8.839%. The third weight change starts at about 850°C with a weight loss of 3.538%. XRD analysis and weight-loss calculations show that the three steps of weight change are associated with the conversion of $\gamma\text{-MnOOH}$ to $\beta\text{-MnO}_2$, then to $\alpha\text{-Mn}_2\text{O}_3$ and finally to Mn_3O_4 , respectively.

Based on the TGA analysis, the calcination process of $\gamma\text{-MnOOH}$ nanorods was further studied with the help of XRD. The results are listed in Table 1. When the calcinations were conducted in air from 250 to 1050°C , the precursor $\gamma\text{-MnOOH}$ changed from $\gamma\text{-MnOOH}$ to $\beta\text{-MnO}_2$, $\beta\text{-MnO}_2$ to $\alpha\text{-Mn}_2\text{O}_3$ and $\alpha\text{-Mn}_2\text{O}_3$ to Mn_3O_4 , and pure phases of $\beta\text{-MnO}_2$, $\alpha\text{-Mn}_2\text{O}_3$ and Mn_3O_4 were obtained, respectively, at 250, 600 and 1000°C . Moreover, when the calcination of $\gamma\text{-MnOOH}$ nanorods was conducted under the flow of N_2 atmosphere, $\gamma\text{-MnOOH}$ was directly converted into Mn_3O_4 at 500°C , which is much lower than that for preparing Mn_3O_4 in air.

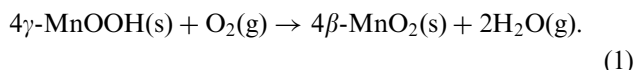
Fig. 2 gives the XRD patterns of the as-prepared products as well as the precursor $\gamma\text{-MnOOH}$ nanorods. Fig. 2A exhibits the XRD pattern of the precursor $\gamma\text{-MnOOH}$ nanorods. Fig. 2B and C show the XRD patterns of the products prepared through heating $\gamma\text{-MnOOH}$ nanorods in air at 350°C for 4 h and at 600°C for 12 h, respectively. The diffraction peaks in patterns B and C can be indexed to pure tetragonal $\beta\text{-MnO}_2$ and pure orthorhombic phase of $\alpha\text{-Mn}_2\text{O}_3$, respectively. Fig. 2D is the XRD pattern of the product resulted from heating $\gamma\text{-MnOOH}$ in N_2 flux at 600°C for 8 h. All diffraction peaks can be indexed to pure tetragonal Mn_3O_4 . The corresponding lattice constants of the as-prepared products are shown in Table 2.

Table 2
Lattice constants of the as-prepared manganese oxides

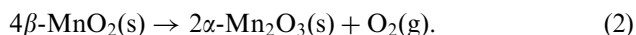
Manganese oxides	Crystal system	Calculated value			Theoretical value			JCPDS card
		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	
β -MnO ₂	Tetragonal	4.4010		2.8700	4.3999		2.8740	No. 24-0735
α -Mn ₂ O ₃	Orthorhombic	9.4080	9.4119	9.4066	9.4161	9.4237	9.4051	No. 24-0508
Mn ₃ O ₄	Tetragonal	5.7680		9.4720	5.7621		9.4696	No. 24-0734

According to our experimental results, the following chemical equations may help to describe the preparation mechanism.

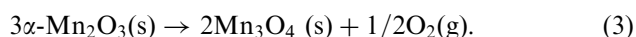
(1) Oxidation of γ -MnOOH to β -MnO₂ in air at 250–550 °C



(2) Decomposition of β -MnO₂ into α -Mn₂O₃ at 550–900 °C

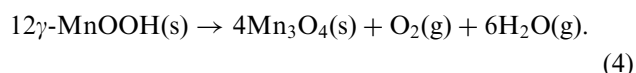


(3) Further decomposition of α -Mn₂O₃ into Mn₃O₄ at above 900 °C



The above manganese oxide phase changes and their transition temperatures are similar to those reported in the literature [29].

(4) Decomposition of γ -MnOOH into Mn₃O₄ in N₂ flux



Different from the case in air, when calcined in N₂ flux, γ -MnOOH can be directly converted into Mn₃O₄ at 500 °C, as described in Eq. (4). Here N₂ flux not only prevents the oxidation of γ -MnOOH by O₂ from the air, but also takes away the O₂ generated from the decomposition reaction (Eq. (4)), and makes the reaction (Eq. (4)) go towards the right side easily. So, under this condition, γ -MnOOH can be directly converted into Mn₃O₄ at 500 °C. This innovation not only saves much energy but also is helpful for Mn₃O₄ sample to retain the nanorod morphology similar to the precursor's, since high-temperature calcination may change or destroy the morphology and structure of the products to some extent, which has been confirmed by TEM observation (see Supplementary materials).

Fig. 3 shows the TEM and HRTEM images of the prepared samples. Fig. 3A is the TEM image of the precursor γ -MnOOH nanorods, with diameters of 20–450 nm and lengths of tens of micrometers. Fig. 3B, C and D show the TEM images of β -MnO₂ prepared in air at 350 °C for 4 h, α -Mn₂O₃ prepared in air at 600 °C for 12 h, and Mn₃O₄ prepared in N₂ atmosphere at 600 °C for 8 h, respectively. The obtained manganese oxides maintain the

1D morphology similar to the precursor γ -MnOOH nanorods, with diameters of tens to hundreds of nanometers and lengths of tens of micrometers. Fig. 3E, F, G and H display the typical nanorod TEM images of γ -MnOOH, β -MnO₂, α -Mn₂O₃ and Mn₃O₄ samples, respectively. The single-crystalline nature of the obtained nanorods can be verified by the corresponding ED patterns (insets in Fig. 3E, F, G and H). The HRTEM images of each nanorod are also displayed correspondingly in the insets of Fig. 3E, F, G and H, showing that the resultant nanorods are structurally uniform. The ED patterns and the HRTEM images of these nanorods help us to get information of the growth. For γ -MnOOH, the interplanar distance of fringes perpendicular to the nanorod axis is 2.88 Å, corresponding to the (101) planes of monoclinic MnOOH. The MnOOH nanorods grow along the [101] crystal direction. For β -MnO₂, the interplanar distance of fringes perpendicular to the nanorod axis is 2.84 Å, corresponding to the (001) planes of tetragonal β -MnO₂, which stands for the growth direction [001]. For α -Mn₂O₃, the interplanar spacing of the fringes marked by arrows is 6.60 Å, corresponding to the ($\bar{1}$ 10) planes of orthorhombic α -Mn₂O₃. The growth direction of the nanorod is along the [101]. For Mn₃O₄, the interplanar spacing of the fringes perpendicular to the rod axis is 3.10 Å, corresponding to the (112) planes of tetragonal Mn₃O₄, which stands for the growth direction [112].

The catalytic performances of the three kinds of manganese oxide nanorods have been studied on the oxidation and decomposition of MB dye with H₂O₂ under controlled conditions. By monitoring the MB absorption at the peak wavelength 664 nm, we obtained the decoloration degree of MB shown in Fig. 4. Here the degree of decoloration is expressed as $(I_0 - I)/I_0$, where I_0 is the absorption at $t = 0$ and I is the absorption at a given reaction time. The three kinds of manganese oxide nanorods have catalytic effects on the oxidation and decomposition of MB with H₂O₂. After 150 min of reaction, the decoloration degree of MB dye for β -MnO₂, Mn₃O₄ and α -Mn₂O₃ nanorod catalysts are about 98%, 85% and 73%, respectively. To prove the catalysis effect, we have done the following comparison experiments (see Supplementary materials). In the absence of any catalysts (only MB + H₂O₂), no obvious dye decoloration is observed after 2 h. With the β -MnO₂ nanorods but no H₂O₂ (only MB + β -MnO₂ nanorods), the degree of decoloration

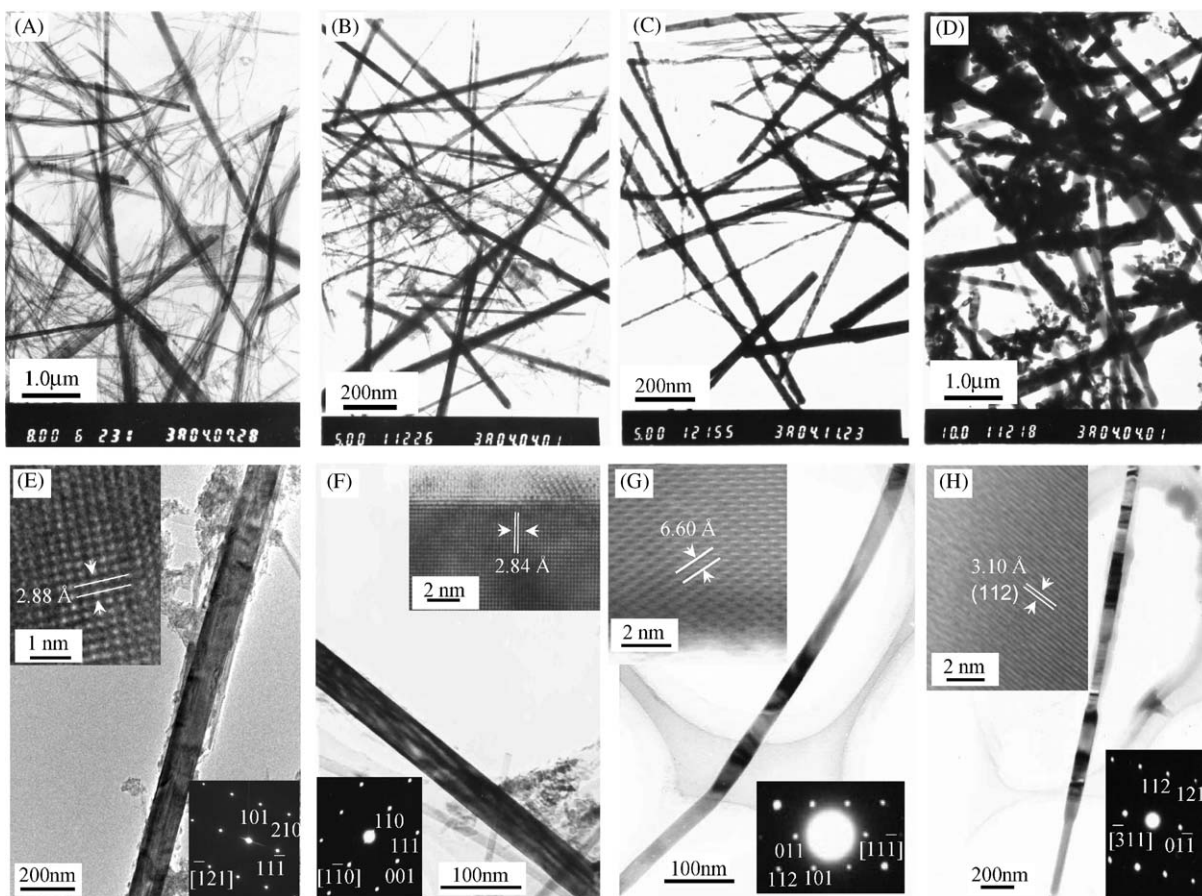


Fig. 3. TEM images of the as-prepared manganese oxides: (A) γ -MnOOH nanorods; (B) β -MnO₂ nanorods; (C) α -Mn₂O₃ nanorods; (D) Mn₃O₄ nanorods; (E) a single MnOOH nanorod, insets are the corresponding SAED pattern and HRTEM image; (F) a single β -MnO₂ nanorod, insets are the corresponding SAED pattern and HRTEM image; (G) a single α -Mn₂O₃ nanorod, insets are the corresponding SAED pattern and HRTEM image; (H) a single Mn₃O₄ nanorod, insets are the corresponding SAED pattern and HRTEM image.

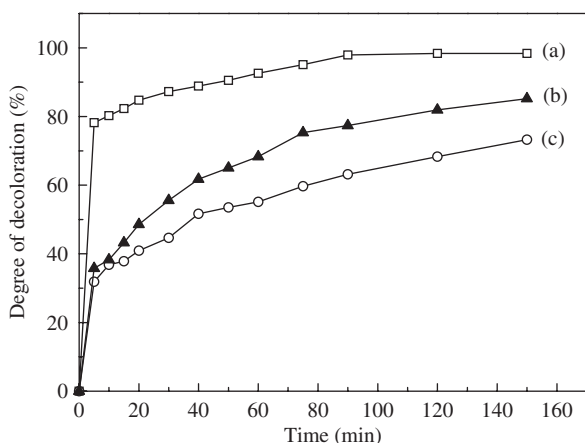


Fig. 4. Time profiles of MB decoloration. (a) MB + H₂O₂ + β -MnO₂ nanorods; (b) MB + H₂O₂ + Mn₃O₄ nanorods; (c) MB + H₂O₂ + α -Mn₂O₃ nanorods.

reaches about 30% within 15 min and then tends to be saturated, which can be ascribed to adsorption of the dye molecules on the β -MnO₂ nanorods. When both β -MnO₂ catalyst and H₂O₂ oxidant were added to the MB solution, obvious decoloration occurred. Remarkably, the use of β -

MnO₂ nanorods as a catalyst increased the degree of decoloration to 82.3% in only 15 min. The saturated degree of decoloration was as high as 98.3%. Catalytic decoloration of MB must have occurred here, because simple adsorption on the surfaces of the nanorods can only account for ~30% of the decoloration. On the other hand, XRD analyses indicate that the manganese oxides have no structure changes before and after the catalytic reactions. The differences in their catalytic activities among the β -MnO₂, Mn₃O₄ and α -Mn₂O₃ nanorod catalysts may result from the difference of their surface areas and active sites. Further investigations on the mechanism of the manganese oxide catalytic reaction are ongoing.

4. Conclusion

In summary, a simple synthetic approach has been used to prepare manganese oxide nanorods. β -MnO₂, α -Mn₂O₃ and Mn₃O₄ nanorods have been obtained, respectively, through calcining γ -MnOOH nanorods in air or under flowing N₂ atmosphere. When the calcinations are conducted in air from 250 to 1050 °C, the precursor γ -MnOOH undergoes the changes from γ -MnOOH to β -MnO₂, then

to α -Mn₂O₃ and finally to Mn₃O₄. When the calcination of γ -MnOOH nanorods is conducted under the flow of N₂ atmosphere, γ -MnOOH can be directly converted into Mn₃O₄ at as low as 500 °C. The obtained manganese oxides maintain the 1D morphology similar to the precursor γ -MnOOH nanorods, with diameters of tens to hundreds of nanometers and lengths of tens of micrometers. The obtained manganese oxide nanorods show catalytic effects on the oxidation and decoloration of the MB dye with H₂O₂. This facile and systematic synthesis method is capable for large-scale preparation of 1D nanostructured manganese oxides and may probably extend to the synthesis of other transition metal oxides.

Acknowledgments

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the on-line version at [doi:10.1016/j.jssc.2005.11.028](https://doi.org/10.1016/j.jssc.2005.11.028)

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