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Abstract: Branched MnOOH nanorods with diameters in the range of 50–150 nm and lengths of up to tens of micrometers were prepared by using potassium permanganate (KMnO$_4$) and PEG 400 (PEG = polyethylene glycol) as starting materials through a simple hydrothermal process at 160°C. After annealing at 300°C under a N$_2$ atmosphere for 5 h, MnOOH nanorods became gradually dehydrated and transformed into mesoporous Mn$_3$O$_4$ nanorods with a slight size-shrinking. The as-obtained mesoporous Mn$_3$O$_4$ nanorods had an average surface area of 32.88 m$^2$ g$^{-1}$ and a mean pore size of 3.7 nm. Through tuning the experimental conditions, such as the annealing atmosphere and temperature, β-MnO$_2$, MnO$_3$, Mn$_3$O$_4$, MnO, and Mn$_5$O$_8$ were selectively produced. Among these structures, mesoporous Mn$_3$O$_4$ nanorods were efficient for the catalytic degradation of methylene blue (MB) in the presence of H$_2$O$_2$ at 80°C.

Keywords: manganese · methylene blue · mesoporous materials · nanostructures · porosity

Introduction

Mesoporous transition-metal oxides have attracted tremendous attention over the past decade, owing to their unique catalytic, electrochemical, magnetic, and adsorptive properties.[1–3] The traditional preparation methods for these mesoporous materials always involve the use of soft templates (typically surfactants, such as triblock copolymer F127, for mesoporous silica or carbon) or hard templates (such as mesoporous silica or anodic alumina, for other mesoporous materials).[4–11] However, soft-template methods usually lead to amorphous frameworks, and hard-template methods require complex procedures.[12–14] Moreover, the scarcity of suitable metallic precursors also limits the application of template methods to prepare most mesoporous transition-metal oxides. Therefore, it is still a great challenge to search for new synthesis methods for porous materials.

The thermal decomposition of hydroxide, carbonate, oxalate, and other metal salts is an effective strategy for synthesizing porous materials.[15–17] By using this method, pores were formed when gases (such as H$_2$O, CO$_2$, and CO) are released during the thermal decomposition of metallic salts. Compared with template methods, this technique does not require complex equipment or tedious post-processing (such as the removal of a template or selective etching in an appropriate solvent), which would introduce impurities and limit the applications of the mesoporous materials. Therefore, such a strategy is more promising than the template methods in industrial manufacturing.

Manganese oxides have been extensively studied because of their outstanding structural flexibility and their physical and chemical properties, such as their catalytic, electrochemical, magnetic, and adsorptive properties. Amongst all of the manganese oxides studied, Mn$_3$O$_4$ is unique owing to its mixed-valence state. Therefore, Mn$_3$O$_4$ has many excellent properties, including as a promising sensor material for detecting volatile organic compounds[18] as an energy-storage material for anodes of lithium-ion batteries, and as an important catalyst in various oxidation and reduction reactions.[19–23] It is well-known that mesoporous materials are more effective than bulk materials when used as catalysts, adsorbents, and energy-storage materials. However, the synthesis of mesoporous Mn$_3$O$_4$ is still a great challenge because Mn$_3$O$_4$ is difficult to synthesize by direct template methods.[3]

Herein, mesoporous Mn$_3$O$_4$ nanorods were synthesized through the thermal decomposition of MnOOH nanorods at low temperatures under a nitrogen atmosphere. These mesoporous Mn$_3$O$_4$ nanorods were characterized by XRD, TEM,
SEM, and HRTEM. Besides these mesoporous Mn$_3$O$_4$ nanorods, β-MnO$_2$, MnO, and Mn$_5$O$_8$ nanorods were also selectively prepared from the thermal decomposition of MnOOH nanorods under different experiment conditions. The catalytic performances of these manganese-oxide nanorods were evaluated in the catalytic oxidation of methylene blue (MB).

**Results and Discussion**

The as-prepared MnOOH and Mn$_3$O$_4$ compounds were characterized by X-ray diffraction (Figure 1). In Figure 1a, all of the diffraction peaks corresponded to monoclinic MnOOH (space group $P2_1/c$, JCPDS card no. 41-1379). This result was supported by the FTIR spectrum (Figure 2a). The peaks at 400–650 cm$^{-1}$ were assigned to Mn–O vibrations, and the peaks at 1083, 1118, and 1155 cm$^{-1}$ were attributed to the out-of-plane bending modes of γ-OH and the in-plane bending modes of δ-2-OH and δ-1-OH, respectively. This spectrum shows the representative bands of the γ-MnOOH phase.$^{[24,25]}$ In Figure 1b, all of the diffraction peaks of the product after calcination at 300°C were indexed to the hausmannite structure of Mn$_3$O$_4$ (space group $I4_1/amd$, JCPDS card no. 24-0734), which agreed with the standard values of bulk Mn$_3$O$_4$. In addition, the peaks were broad and weak, owing to the poor crystallinity or the small crystal domain in the product, which resulted from the low preparation temperature. The FTIR spectrum (Figure 2b) also confirmed that the sample was manganese oxide. The peaks centered at 417, 481, and 602 cm$^{-1}$ were maintained in the FTIR spectrum, but the peaks owing to the O–H group disappeared, thus indicating its absence in the product. This result was in good agreement with the identification of the product as Mn$_3$O$_4$.

Figure 3 shows the field-emission SEM (FESEM) images of the as-obtained MnOOH and Mn$_3$O$_4$. Most of the MnOOH particles displayed typical rod-like shapes and smooth surfaces (Figure 3a,b). The diameters of these nanorods were in the range 50–150 nm and their lengths were up to tens of micrometers. Many nanorods grew on the surface.
of the other nanorods, thereby producing branch-like trees. This branched rod-like feature was also observed by TEM (Figure 4a). The HRTEM image (Figure 4b) shows clear lattice fringes of 0.25 nm and 0.48 nm, which corresponded to the [111] and [110] crystal planes of MnOOH, respectively. The branched rod-like feature was also observed in the Mn₃O₄ particles after the calcination of the MnOOH nanorods at 300°C (Figure 3c,d). However, the surface of the Mn₃O₄ nanorods became rough and some pore-like structures appeared on the surface, which was confirmed by pore-size measurements and TEM analysis. The diameter of these Mn₃O₄ nanorods was slightly smaller than before the calcination, which was attributed to a shrinkage caused by the decomposition of MnOOH. TEM analysis of the Mn₃O₄ nanorods also showed the existence of the pores (d = 2–5 nm), which were distributed throughout the whole of the nanorods (based on the contrast difference; Figure 4c). A HRTEM image of a mesoporous Mn₃O₄ nanorod showed a distance between neighboring lattice fringes of about 0.31 nm, which was attributed to the [112] crystal plane of tetragonal Mn₃O₄ (Figure 4d).

The nitrogen-adsorption/desorption isotherms of MnOOH and Mn₃O₄ are shown in Figure 5. MnOOH exhibited an isotherm of type II (Figure 5a), which was the normal form of isotherms gained with a non-porous or macroporous adsorbent. The surface area was only 8.5 m² g⁻¹. However, the Mn₃O₄ sample showed an isotherm of type IV (Figure 5b). The hysteresis loops did not close at P/P₀ < 1 and such results are often ascribed to the aggregates of nanoparticles. The Mn₃O₄ sample had a high surface area of 32.88 m² g⁻¹. The total pore volume was 0.053 m³ g⁻¹. The pore-size distribution (Figure 6), which was calculated by using (N₂) original density functional theory (DFT) assuming slit-pore geometry suggested micro- and mesoporosity. BJH desorption gave an average pore-width of 3.7 nm, which was in agreement with the TEM observations. This result was due to the conversion of MnOOH into Mn₃O₄ with a significant loss of oxygen and hydrogen, during which the pore-formation occurred. Therefore, the surface area of Mn₃O₄ was much larger than that of MnOOH.

A series of contrast experiments were carried out to investigate the effects of the reaction parameters on the mesoporous Mn₃O₄ nanorods. Because the mesoporous Mn₃O₄ nanorods were prepared by a hydrothermal reaction, followed by thermal annealing, these two processes were investigated separately. First, the effect of the reaction temperature on the hydrothermal reaction was investigated: If the temperature was below 120°C, only nanoparticles were obtained. At 160°C, branched MnOOH nanorods were produced. At 180°C, coexistence of Mn₃O₄ nanoparticles with MnOOH was observed in the final products. Besides the reaction temperature, the reaction time also played an important role in the formation of branched MnOOH. The longer
the reaction time (up to 5 h), the larger the amount of branched MnOOH nanorods obtained; after 5 h, their yield remained almost unchanged. PEG 400 was one of the essential reagents for the formation of branched MnOOH nanorods. When PEG 400 was replaced by poly(4-vinylphenol) (PVP) or sodium dodecylbenzenesulfonate (SDBS), branched nanorods were not observed. We also investigated the formation of branched MnOOH nanorods. Nanoparticles were formed during the initial stages of the reaction (see the Supporting Information, Figure S4a) and then grew into coarse nanorods with increased reaction time (see the Supporting Information, Figure S4b). The coarse nanorods turned into smooth nanorods with small nanorods attached onto their surfaces (see the Supporting Information, Figure S4c). With further prolonged reaction time, the attached nanorods grew into branched nanorods (see the Supporting Information, Figure S4d). Based on these above experimental results, we considered that PEG 400 played a pivotal role in the formation of the MnOOH nanorods during the early stages of the reaction. As PEG 400 is a nonionic surfactant with uniform, ordered chain-structure and has multiple coordinating sites, it was easily adsorbed onto the surface of the metal-oxide colloid during the synthesis, thereby confining the colloid and facilitating the anisotropic growth of the 1D nanocrystals.[27,28,29] With a prolonged reaction time, the diameters and lengths of these nanorods increased notably. To reduce the total interfacial energy of the system, large amounts of these nanorods tended to aggregate and grow into branched structures. This self-assembly process was similar to that reported previously.[30] Finally, branched nanorods were obtained in high yields.

It is well-known that metal hydroxides can be converted into their corresponding oxides by thermal annealing. The annealing parameters (e.g., temperature, reaction time, and atmosphere) are critical for controlling the phase and morphology of the final products. Therefore, we studied the thermal-annealing behavior of MnOOH under air and nitrogen atmospheres, respectively. The TGA curves of MnOOH under N₂ and air atmospheres are shown in Figure 7a,b. First, MnOOH decomposed into β-MnO₂ (see the Supporting Information, Figures S1d and S2b) between 250 and 280°C. Then, β-MnO₂ released oxygen and turned into Mn₃O₄ (see the Supporting Information, Figures S1a and S2c) between 550 and 600°C. Finally, Mn₃O₄ released more oxygen and changed into MnO between 930 and 950°C (see the Supporting Information, Figures S1b and S2e). The weight losses of the corresponding parts were 1.65 %, 10.38 %, and 13.1 %, which were close to the theoretical values of 1.13 %, 10.22 %, and 13.25 %, respectively (Figure 7b). This pattern is typical of the decomposition of MnOOH in air.[31] However, the TGA curve under a N₂ atmosphere was different. First, MnOOH decomposed into Mn₃O₄, then into MnO₂, and finally into MnO (see the Supporting Information, Figures S1e and S2d). The weight-loss of every step was also consistent with the theoretical value. This process was the same as in most of the previous reports.[31,32] However, when MnOOH nanorods were annealed at 300°C for 2 h under a nitrogen atmosphere, Mn₃O₄ nanorods were obtained (see the Supporting Information, Figures S1c and S2a). Mesoporous Mn₃O₄ nanorods were formed after 5 h. The latter process was not reflected in the TGA curve, presumably because the decomposition of MnOOH was a very slow process at low temperatures and the TGA test was a very fast heating process (heating rate: 10°C/min⁻¹). Therefore, some of the slow-decomposition process could not be detected in the TGA curve. To further investigate the decomposition behavior of MnOOH under a nitrogen atmosphere, a fine-TGA test was carried out at 300°C (Figure 8). MnOOH gradually decomposed over 5 h at 300°C under a N₂ atmosphere, and the weight loss was 13.2 %, which agreed with the theoretical value of Mn₃O₄.
13.25% for decomposition into Mn$_3$O$_4$. Therefore, the decomposition process of MnOOH at 300°C under a N$_2$ atmosphere can be represented as given in Equation (1):

$$\text{MnOOH} \rightarrow \text{Mn}_3\text{O}_4$$

First, MnOOH decomposed into Mn$_5$O$_8$ and then into Mn$_3$O$_4$ as the annealing time increased. Low synthesis temperatures did not destroy the pores that formed during the decomposition process. Therefore, the mesoporous Mn$_3$O$_4$ nanorods were obtained.

The as-obtained mesoporous Mn$_3$O$_4$ nanorods were used as a catalyst for waste-water treatment. MB, as a typical industrial pollutant, was chosen as a model to examine the catalytic performance of the mesoporous Mn$_3$O$_4$ nanorods. As the degradation of MB proceeds, the characteristic absorption of MB at 665 nm gradually weakens, which was why it was chosen for monitoring the catalytic process of mesoporous Mn$_3$O$_4$ nanorods. The catalytic performance of mesoporous Mn$_3$O$_4$ in the presence of H$_2$O$_2$ is shown in Figure 9. The initial spectrum showed four absorption peaks (245, 292, 614, and 664 nm), which originated from the molecular absorption of MB.[32] The intensities of these peaks quickly decreased within 10 min. The MB bands at 292 and 245 nm were covered by the strong absorption of hydrogen peroxide. As the reaction proceeded, the color of the solution slowly changed from dark blue to colorless. No obvious new band was observed in the spectrum (Figure 9), thereby suggesting the complete degradation of the MB molecules.

The degradation efficiency of the MB molecules was calculated by $\frac{I_0 - I}{I_0}$, where $I_0$ was the absorbance at 665 nm at $t = 0$ and $I$ was the absorbance at the same wavelength at a given reaction time. The degradation efficiency of the as-prepared mesoporous Mn$_3$O$_4$ nanorods was 95% after 1 h and 99.8% after 2 h (Figure 10d), which was slightly more effective than the Mn$_3$O$_4$ nanorods (prepared herein; Figure 10c), Mn$_3$O$_4$ octahedra, and MnO$_2$ nanorods.[33–35] The good catalytic performance of the mesoporous Mn$_3$O$_4$ nanorods may have been due to the mesoporous (high surface area) and 1D structures (high surface-to-volume ratio). No obvious decolorization was observed without Mn$_3$O$_4$ or H$_2$O$_2$, even after 2 h (Figure 10a,b).[33] which indicated that the degradation of MB molecules was caused by H$_2$O$_2$-induced oxidation, catalyzed by Mn$_3$O$_4$.

Our preliminary experiments have shown a relatively high energy-storage capacity of mesoporous Mn$_3$O$_4$ nanorods in lithium-ion batteries (560 mAh g$^{-1}$ after 35 cycles at 50 mAg$^{-1}$; see the Supporting Information, Figure S3). This value is larger than those of Mn$_3$O$_4$ nanofibers (450–500 mAh g$^{-1}$) and MnO/C composites (200–300 mAh g$^{-1}$).[36,37] This result was ascribed to the mesoporous (high surface area that allowed the electrode and the electrolyte with sufficient contact area) and 1D structures (1D electron-transport pathways) of the mesoporous Mn$_3$O$_4$ nanorods.[38]

Conclusion

Branched MnOOH nanorods were successfully synthesized by using a simple and mild hydrothermal procedure. The anisotropic growth of MnOOH was attributed to the PEG-assisted oriented attachment of nanocrystalline material. Mesoporous Mn$_3$O$_4$ and other kinds of branched manganese oxides (β-MnO$_2$, Mn$_3$O$_5$, MnO, and Mn$_3$O$_6$) were obtained as desired by performing the heat treatment of the MnOOH precursor under different temperatures and atmospheres. The as-obtained mesoporous Mn$_3$O$_4$ nanorods exhibited effective catalysis for oxidative decomposition of MB and high energy-storage capacity in lithium-ion batteries.
**Experimental Section**

**Synthesis of mesoporous nanorods Mn$_3$O$_4$:** All of the reagents were analytical grade and used without further purification. In a typical synthesis of branched MnOOH nanorods, PEG 400 (2 mL) and potassium permanganate (KMnO$_4$) (0.1 g) were mixed together and placed into a 60 mL Teflon cup. Distilled water was added up to 70% of the total volume under violent magnetic agitation. Next, the Teflon-lined autoclave was sealed tightly and was heated at 160°C for 5 h, before being allowed to cool to room temperature. The precipitates were collected by filtration, washed several times with distilled water and absolute EtOH, and finally dried at 60°C for 5 h. The as-prepared precipitate was calcined at 300°C under a N$_2$ atmosphere for 5 h to afford mesoporous Mn$_3$O$_4$ nanorods. For details of the synthesis other manganese oxides (Mn$_3$O$_4$, MnO, and Mn$_5$O$_8$), see the Supporting Information, Table S1.

**Catalytic oxidation reaction:** The catalysis experiment was carried out in a 250 mL glass flask that contained an aqueous MB solution (100 mg/L, 5 mL) at 80°C under a N$_2$ atmosphere for 5 h to afford mesoporous Mn$_3$O$_4$ nanorods. For details of the synthesis other manganese oxides (Mn$_3$O$_4$, MnO, and Mn$_5$O$_8$), see the Supporting Information, Table S1.

**Instruments:** X-ray powder diffraction (XRD) patterns were obtained from a Bruker D8 advanced X-ray diffractometer that was equipped with graphite-monochromated CuKα radiation (λ = 1.5418 Å). Field-emission scanning electron microscopy (FESEM) images were taken with a JEOL JSM-7600F field-emission instrument. High-resolution TEM (HRTEM) images were recorded on a JEOL-2100 high-resolution transmission electron microscope at an acceleration voltage of 200 kV. PXRD spectra were measured on a Shimadzu FTIR-8400S spectrometer. Thermal gravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA851 thermal analyzer apparatus under air and N$_2$ flows, respectively. Nitrogen sorption measurements were performed on a Tristar II 3020 gas sorptometer. Samples were degassed to 0.003 mm Hg for 12 h at 60°C. Specific surface areas were calculated by using the Brunauer-Emmett-Teller (BET) method, and pore sizes and volumes were estimated from pore-size distribution curves from the adsorption branches of the isotherms. Absorption spectra were measured with a TU-1901 UV/Vis spectrophotometer.

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