Shape-Controlled Synthesis of One-Dimensional MnO₂ via a Facile Quick-Precipitation Procedure and its Electrochemical Properties

Sheng Chen, Junwu Zhu,* Qiaofeng Han, Zhijun Zheng, Yong Yang, and Xin Wang*

Key Laboratory for Soft Chemistry and Functional Materials (Nanjing University of Science and Technology), Ministry of Education, Nanjing 210094, China

Received February 21, 2009; Revised Manuscript Received July 9, 2009

ABSTRACT: MnO₂ with different crystallographic forms (α, γ) and morphologies (needles, rods, and spindles) was fabricated via a facile quick-precipitation procedure at a low temperature (about 83 °C) without using any templates or surfactants. The proposed mechanism is focused on the different reaction parameters that affect the behaviors of MnO₆octahedron units (basic structural framework of MnO₂), which then exert an influence on the formation and stack of nuclei in the crystal growth process. Specific capacitances (Cₛ) calculated according to the area of the cyclic voltammograms (CV) curves were 233.5, 83.1 F·g⁻¹ for the needle- and 95.5, 29.3 F·g⁻¹ for the spindle-like products at the scan rate of 5, 100 mV·s⁻¹, respectively. The Cₛ of needle-like samples calculated by discharge curves at the current density of 2 mA·cm⁻² is 209.8 F·g⁻¹, close to the value calculated by CV curves at the scan rate of 5 mV·s⁻¹. This methodology facilitates us to synthesize MnO₂ with discrepant one-dimensional (1D) nanostructures via a quick, simple, and mild route and may be readily extended to the preparation of many other oxide nanoparticles.

1. Introduction

Manganese dioxide (MnO₂), one of the most stable manganese oxides with excellent physical and chemical properties under ambient conditions, is environmentally compatible, low cost, and abundant in nature.¹⁻⁴ Because of its rich polymorphism and structural flexibility, this oxide has wide applications in catalysis, ion exchange, molecular absorption, microwave absorption, biosensors, and energy storage.⁵⁻⁷

Recently, considerable attention has been directed toward nanoscale morphologies owing to their unique optical, magnetic, mechanical, and electronic behaviors.⁸ Among them, low dimensionality nanostructures, for instance, one-dimensional (1D), exhibit specific behavior.⁹⁻¹²

A variety of preparation techniques have been exploited to synthesize 1D MnO₂ with discrepant shapes, for example, hydrothermal,¹³ reflux,¹⁴ sol–gel,¹⁵ precipitation,¹⁶ sonication,¹⁷ electrodeposition,¹⁸ etc. In previous work, synthesis of rod- and needle-like MnO₂ was achieved via a hydrothermal and reflux procedure by Wang et al.¹³ and Villegas et al.,¹⁴ respectively; Liu et al.¹⁵ addressed a sol–gel-assisted solid-state route employing different cross-linking reagents (polyvinyl acetate, glycerol, or glucose) and obtained MnO₂ with rod-, needle-, and wire-shapes. In addition, an aqueous precipitation method was developed by Portehault and co-workers¹⁶ to fabricate MnO₂ nanowires; Kumar et al.¹⁷ demonstrated that MnO₂ nanoneedles can also be obtained by sonication of MnO₂·3H₂O for 3.5 h, and Li et al.¹⁸ reported a one-step electrodeposition method for preparing α-MnO₂ nanowires. However, intricate operations, introduction of cross-linking reagents, long reaction time, and expensive equipment seem to be great obstacles for their commercialization. Therefore, development of quick, simple, and mild pathways for the synthesis of MnO₂ with 1D morphologies still remains a great challenge.

In this paper, we describe a facile quick-precipitation procedure to fabricate MnO₂ with different crystallographic forms (α, γ) and morphologies (needles, rods, and spindles). To our best knowledge, little work on synthesis of needle- and spindle-like MnO₂ via precipitation of Mn²⁺ and Mn⁷⁺ in water-isopropanol reacting system has been reported. Considering the polarity, effect of steric hindrance, and electrostatic effect, etc., generally the coordination capability of water species should be larger than that of the isopropanol, and thus there is a competition reaction of the coordination between water molecules and isopropanol, which eventually affected the morphology and texture of as-obtained products; therefore, the introduction of a double solvent system would provide a wider space for us to manipulate the properties of the products. Taking into account that many properties (e.g., electrochemical, catalytic, or magnetic) of MnO₂ depend heavily on its morphology and texture, our procedure enables us to manipulate its properties effortlessly. Some remarkable advantages of our method compared with others are its facile operation condition, simple apparatus, and short reaction time, which are of great value from the viewpoint of commercialization. The possible growth mechanisms of these nanostructures have been studied based on the experimental results. Furthermore, as a potential excellent electrode material for supercapacitors,¹⁹ the electrochemical properties of as-obtained products are also investigated under a three-electrode cell configuration at room temperature.

2. Experimental Section

2.1. Synthesis of 1D MnO₂ Nanostructures. All chemical reagents were analytical grade and used as received. In a typical process for the preparation of needle-like MnO₂, MnCl₂·4H₂O (0.18 g) was mixed with isopropanol (50 mL) in a round-bottomed flask equipped with a refluxing apparatus. The solution was heated to approximately 83 °C with vigorous stirring, and then KMnO₄ (0.10 g) dissolved in 5 mL of deionized (DI) water was added into the above boiling solution rapidly, where a large amount of black precipitate was simultaneously produced. Ten minutes later, the
mixture was cooled to room temperature. After centrifugation and washing with DI-water, the precipitate was dried at 60 °C in air overnight.

The whole process can be conveniently adjusted to prepare spindle-like products when 5 mL of DI-water was replaced by 20 mL of DI-water. However, when KMnO₄ (0.033 g) was dissolved in DI-water (5 mL), and dropped slowly (with a duration of about 30 min) into the boiling solution comprising of MnCl₂·4H₂O (0.06 g) and isopropanol (50 mL), MnO₂ with rod-like shapes can be obtained.

2.2. Material Characterization. Powder X-ray diffraction (XRD) analyses were performed on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ ≈ 1.54 Å) at a slow scan rate of 0.01°/s for the careful examination of the crystalline phase structure. UV–vis absorption and/or transmission spectra were obtained using a BRAIC UV-1201 spectrophotometer. Morphologies of as-obtained products were observed on a transmission electron microscope (TEM, JEOL JEM-2100) and field emission scanning electron microscopy (FESEM, Hitachi S-4800). The products dispersed in DI-water were subjected to sonication for a few minutes and then dropped onto a 200 mesh Cu grid having a holey carbon support film. To investigate the mechanism of the overall procedure, a droplet of product was taken separately from the reaction mixture at different times for TEM observation.

2.3. Electrochemical Measurement. The working electrodes were fabricated by mixing the prepared powders with 15 wt % acetylene black and 5 wt % polytetrafluorene-ethylene (PTFE) binder. A small amount of DI-water was added to the mixture to produce a homogeneous paste. The mixture was pressed onto nickel foam current-collectors (1.0 × 1.0 cm) to make electrodes. Before the electrochemical test, the prepared electrode was soaked overnight in 1 M Na₂SO₄ solution. Electrochemical characterization was carried out in a conventional three-electrode cell with 1 M Na₂SO₄ as the electrolyte. Platinum foil and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All electrochemical measurements were conducted on a CHI 660B electrochemical workstation (Shanghai CH Instrument Company, China).

3. Results and Discussion

3.1. Structure Characterization. The XRD patterns of the obtained MnO₂ products are shown in Figure 1. Almost all the diffraction peaks of needle- and rod-like products can be assigned to the tetragonal phase of α-MnO₂ (JCPDS 44-0141, a = 9.7845 Å, c = 2.8630 Å), while the peaks of spindle-like products are indexed to the orthorhombic phase of γ-MnO₂ (JCPDS 14-0644, a = 6.36 Å, b = 10.15 Å, c = 4.09 Å). No peaks attributable to manganese oxides with other crystallographic forms are observed, indicating the high purity of as-obtained products. Besides, the line broadening observed in the XRD patterns suggests these samples are in a poor crystalline state with a short-range crystal form.

Figure 1. XRD patterns of the obtained needle-, rod-, and spindle-like products.

Such low degree of the crystallinity can be attributed to the rapid addition of KMnO₄. Since KMnO₄ was added at a relative higher temperature (about 83 °C), and the reaction rate was higher, causing a large amount of nuclei to form in a short time and leaving the crystals to grow inadequately, thus all the obtained products were in a poor crystalline phase. The XRD patterns indicate that MnO₂ with different crystallographic forms (α, γ) can be obtained under current synthetic conditions.

3.2. Morphology of the Products. Interesting morphologies of as-obtained products were observed with TEM and FESEM. As can be seen from the overall view (Figure 2a, d,g), the obtained three samples dispersed on the TEM grids show needle-, rod-, and spindle-like morphologies, with diameters of 20–50 nm, 40–100 nm, 30–80 nm and lengths...
of 200−500 nm, 100−200 nm, 70−160 nm, respectively, which is consistent with FESEM images as shown in Figure 3.

To get more structural information about the needle- and rod-like products, the tip of these samples was observed with HRTEM and displayed in the inset of (a) and (d) and in Figure 1S (Supporting Information). It can be clearly seen from these images that the synthesized needle- and rod-like samples are actually composed of a few primary nanorods aggregated along the lateral faces; the nanorods in the center of needle-like samples are longer than other portions, while those of rod-like samples shared an approximately equivalent length. This phenomenon is very consistent with our proposed mechanism.

Moreover, Figure 2c,f,h reveals another delicate difference of the obtained products. As shown in Figure 2c, the nanoneedle is composed of three (or more) primary nanorods (approximately 10 nm width) aggregated along the lateral faces. This observation is consistent with XRD data because the crystallite width is on the order of primary particle diameters. Lattice fringes running along the nanoneedle axis are identical for both primary particles, indicating good alignment of the primary nanorods along a direction perpendicular to the needle axis. The lattice spacing of about 0.70 nm between adjacent lattice corresponds to the distance between two (110) crystal planes of $\gamma$-MnO$_2$. A similar situation observed on HRTEM for the nanorod (Figure 2g) suggests the as-obtained rod-like samples also bear $\alpha$-type crystal form. Nevertheless, Figure 2h reveals that the spindle-like products grow in a random pattern with lattice spacing of approximately 0.40 nm, corresponding to the distance between two (120) crystal planes of $\gamma$-MnO$_2$, which could be explained by the random intergrowth of ramsdellite and pyrolusite domains in the construction of $\gamma$-MnO$_2$. All of these phenomena agree well with XRD data, implying MnO$_2$ with different crystallographic forms ($\alpha$, $\gamma$) and morphologies (needles, rods, and spindles) can be obtained by this method.

3.3. Formation of 1D MnO$_2$ Nanostructures. To investigate the formation process of the needle-like products, some of their intermediates were collected and observed by TEM. As shown in Figure 4a, the intermediates, which were obtained by taken directly from the reacting mixture with the reaction duration of 10 s, are mainly disordered precursors consisting of a small amount of nanoneedles. Figure 4b,c shows TEM images of intermediates obtained by taken directly from the reacting mixture with the reaction duration of 1 and 3 min, respectively; the disordered precursors gradually disappear with the emergence of more needle-like products, indicating a transformation process of disordered precursor into nanorods via a dissolution−crystallization mechanism. Until now, it is safe for us to conclude that two mechanisms are responsible for the particle sizes increment: (a) a dissolution−crystallization process which converts less ordered precursors into primary nanorods, and (b) an oriented attachment process which aggregates primary nanorods along the lateral faces to form needle-like products. It should be noted that the morphology for samples with a longer reaction time, such as 5, 10, 30, and 60 min, displays no pronounced distinction (Figure 2S, Supporting Information) and also the incremental of the yield of the product becomes insignificant (from 80.5% to 89.5%, Table 1S, Supporting Information). These facts suggest that the crystal growth process has almost been completed after a reaction time of 5 min.

To have a further understanding of the formation mechanism, UV−vis spectroscopy was employed to monitor the whole procedure. As observed in Figure 5, the absorption peak of MnO$_2$ gradually redshifs from 383.2 to 403.4 nm when the reaction time was elongated from 10 s to 3 min, due to the increased particle sizes of the products. In addition, no obvious red shift of the absorption peaks was observed after 5 min, providing more evidence for the completeness of the reaction.

Another essential character for our system is that some reaction parameters such as the ratio of DI-water/isopropanol, and the addition and concentration of KMnO$_4$ solution, play an important role in governing the morphology of the prepared products. Specifically, the former contributes to the structural differences of the intermediate species for crystal growth due to the discrepant coordinate abilities
between DI-water and isopropanol with MnO$_6$ octahedron units, while the latter affects the stacking behavior of the nuclei during the crystal growth period.

On the basis of our experimental results, a mechanism, as shown in Scheme 1, is put forward to interpret the formation of as-obtained 1D MnO$_2$ nanostructures (Scheme 1). The structural framework of MnO$_2$ is made of basic MnO$_6$ octahedron units, which are linked in different ways to produce MnO$_2$ crystals with discrepant crystallographic forms and morphologies.\textsuperscript{23,24}

At the initial stage, a large amount of nuclei were formed in a short time from the redox reaction occurring between Mn$^{2+}$ and Mn$^{7+}$ at a relative higher temperature (about 83 °C). Then, different ratios of DI-water/isopropanol can lead to discrepant coordination manners between H$_2$O and isopropanol molecules with O atoms in units of the MnO$_6$ octahedrons. Since (001) faces are the most energetic ones,\textsuperscript{16} H$_2$O molecules, which coordinate with MnO$_6$ octahedron units more easily than isopropanol when considering the polarity, effect of steric hindrance, electrostatic effect, etc.,\textsuperscript{25} will bind with O atoms of MnO$_6$ octahedra in this direction in priority. Therefore, with the addition of a small amount of water (DI-water: isopropanol = 5 mL: 50 mL), H$_2$O molecules interact with only the O atoms along the (001) direction; however, the interaction of H$_2$O molecules with O atoms of MnO$_6$ octahedra in other directions becomes possible when more water is introduced (DI-water/isopropanol = 20 mL/50 mL).

It should be noted that the coordination of H$_2$O and isopropanol with O atoms of MnO$_6$ has a discrepant effect on further packing behavior of the crystal growing species. The intermolecular hydrogen bindings formed between H$_2$O coordinated species makes the following procedure, both thermodynamically and kinetically, favorable to form highly ordered aggregates, whereas shortage of such strong intermolecular interactions in isopropanol coordinated species makes the crystal stacking inclined to be disordered. As a result, in cases when less water (5 mL) is introduced, the overall system has one and only one preferable crystal growth direction; that is, the (001) direction and therefore needle- or rod-like products are produced. On the contrary, crystal growth not only along the (001) direction, but also other directions such as those along the octahedral plane, becomes feasible when more water (20 mL) is added, and thus a spindle-like MnO$_2$ is produced eventually.

To have a better understanding of the role of water and isopropanol in the double system, a control experiment was conducted in which the overall crystal growth procedure takes place in a water and isopropanol, respectively. A repeated experiment confirms that only nonuniform particle-aggregates can be obtained when water is used as the solvent (Figure 3Sa, Supporting Information); on the contrary, almost no MnO$_2$ was prepared in the case of the isopropanol system which can be attributed to the absence of water species (In the reaction 2KMnO$_4$ + 3MnCl$_2$ + 2H$_2$O $\rightarrow$ 5MnO$_2$ + 2KCl + 4HCl, water is one of the required reagents in producing the desired product). It is worth mentioning that the addition of 50 mL of water in this system results in the formation of more bondings between H$_2$O and O atoms of MnO$_6$ units, and thus a series of the interactions between H$_2$O molecules with O atoms of MnO$_6$ units lead the products to exhibit discrepant morphologies, such as needle-aggregates, pseudospindles, and particles, etc. (Figure 3Sb, Supporting Information).

Moreover, the addition and concentration of KMnO$_4$ solution exert a synergic effect on the formation and stacking of the nuclei in the crystal growth process. A rapid introduction of KMnO$_4$ solution with higher concentration (20 mg·mL$^{-1}$) causes the formation of a large amount of growing species in a short time. Considering dissolution–crystallization and oriented attachment are two simultaneous processes in the crystal growth,\textsuperscript{16} and that kinetically the center of the primary nanorods has a higher growing speed compared with the other directions, needle-like products are formed in the end. In great contrast, the slow addition of KMnO$_4$ solution with a relative lower concentration (6.6 mg·mL$^{-1}$) in a dropwise manner causes the formation and stacking of the nuclei at a relatively comparable rate. Consequently, no pronounced difference between the central parts and other portions can be observed, which leads to primary nanorods with an approximately equivalent length, producing the rod-like products.

Furthermore, we have conducted some control experiments to get a better understanding of the effects of the concentration and dropping velocity on the growth of the rod-like samples. TEM images of the samples prepared when the dropping rate of KMnO$_4$ solution is 0.3 and 0.5 mL·min$^{-1}$ with the concentration unchanged (6.6 mg·mL$^{-1}$), and when the concentration
is 20 mg·mL$^{-1}$ and the dropping velocity is not changed (0.1 mL·min$^{-1}$) are shown in Figures 4S and 5S (Supporting Information); these products are no longer nanorods but pseudonanoneedles. We speculate that the slower dropwise addition of K$_2$MnO$_4$ solution with higher concentration, similar to the rapid addition of it with a lower concentration, would lead a higher concentration of the crystal species; as a result, kinetically, the primary nanorods in the center hold a relative higher growing speed compared with the other portions (but lower than that of needle-like samples), producing the pseudo-
needle-like products in the end. Further study on the growth mechanism and the effects of other reaction parameters (such as solvents, manganese precursors, concentrations, reaction time, and pH) is still in progress.

3.4. Electrochemical Properties. The electrochemical properties of as-prepared samples are investigated under a three-electrode cell configuration. Of all the metal oxides studied as pseudocapacitor materials (such as RuO$_2$, IrO$_2$, NiO, CoO$_x$, SnO$_2$, and MnO$_2$), hydrated RuO$_2$ has been found to be most promising because of its excellent electrochemical behavior with larger specific capacitance ($C_s$), greater reversibility, and better stability, but some disadvantages such as low nature abundance, high cost, and the requirement of employing highly acidic solutions (such as sulfuric acid) as electrolyte have prevented its widespread application.

As a low-cost replacement for hydrated RuO$_2$, MnO$_2$ has raised much interest recently because of its abundant availability on the Earth. Besides, MnO$_2$ shows good electrochemical performance in a neutral electrolyte (such as Na$_2$SO$_4$, K$_2$SO$_4$, and LiCl), which would be noteworthy when focused on an ecofriendly point of view. As recently demonstrated, the electrochemical performance of MnO$_2$ critically depends on their crystallographic forms and then on their textural properties including morphology, surface area, pore volume, pore dimension, etc.

Because of the α-type nature of as-obtained needle- and rod-like products, they share a similar (2 × 2) tunnel structure, as pointed out by Devaraj and co-workers recently, seldom discrepancy in electrochemical performance should occur and indeed has been observed in the electrochemical test. But the synthetic process of the rod-like products holds numerous disadvantages including low quantity, long reaction time, etc., which would inhibit its further utilization. Thus, only the results of needle- and spindle-like products are displayed in this paper. Besides, the results of bulk MnO$_2$ are also presented here for comparison.

Typical CV curves were recorded at a scan rate of 5 and 100 mV·s$^{-1}$ in 1 M Na$_2$SO$_4$ at room temperature, with a loading level of 4.0, 8.1, and 5.5 mg·cm$^{-2}$ for needle-like, spindle-like, and bulk MnO$_2$, respectively. As shown in Figure 6a, the rectangle-like CV curves of the needle- and spindle-like products reveal the perfect electrochemical capacitive behaviors of the synthesized samples. The curves show no obvious peaks, indicating that the electrode charged and discharged at a pseudoconstant rate over the whole volumetric cycle. Average specific capacitances ($C_s$) calculated according to the area of the CV curves are 233.5 F·g$^{-1}$ for the needle-like, 95.5 F·g$^{-1}$ for the spindle-like, and 29.1 F·g$^{-1}$ for the bulk products. The discrepancy between needle- and spindle-like samples may be ascribable to different crystallographic forms to provide discrepant gaps for accommodation of alkaline ions. As is well-known, α-MnO$_2$ has a 1D structure and (0.46 × 0.46 nm) tunnels, alkaline cations (such as Na$^+$ with a size of 0.4 nm in aqueous solution) thus can be readily intercalated into the wide tunnels, but the (0.46 × 0.23 nm) tunnels of γ-MnO$_2$ can only alternatively accommodate these ions, resulting in a relative lower specific capacitance. In addition, the $C_s$ of as-obtained needle-like samples is much higher than the bulk MnO$_2$, suggesting the advantage of nanoscale materials over their bulk counterpart, owing to the novel shape- and size-dependent properties appearing on the nanoscale.

The CV curves recorded at a scan rate of 100 mV·s$^{-1}$ (Figure 6b) shows a similar situation. The $C_s$ are calculated to be 83.1, 29.3, and 11.2 F·g$^{-1}$ for the needle- like, spindle- like, and bulk samples, respectively. Since the redox reactions depend on the insertion–deinsertion of alkali ion from the electrolyte, at low scan rates (5 mV·s$^{-1}$), the diffusion of ions from the electrolyte can gain access to almost all available pores of the electrode, leading to a complete insertion reaction, and therefore, it shows almost ideal capacitive behavior. However, with the scan rate increasing, the effective interaction between the ions and the electrode is greatly reduced, and hence, the deviation from rectangularity of the CV becomes obvious, and there is a reduction in capacitance.

On the basis of the above results, further charge–discharge performance measurements were focused on the needle-like MnO$_2$, which were carried out in 1 M Na$_2$SO$_4$, with a loading level of 7.6 mg·cm$^{-2}$ at a current density of 2 mA·cm$^{-2}$. As shown in Figure 7, during the charging and discharging steps, the charging curves are very symmetric to their discharging counterparts in the whole potential region and the slope of every curve is potential-independent and maintained a constant value, indicating its excellent pseudocapacitance behavior. The $C_s$ is calculated according to $C_s = I \times \Delta V / (\Delta t \times m)$ from the discharge curves, where the $I$ is the constant discharge current, $\Delta t$ is the discharge time, $\Delta V$ is the potential drop during discharge, and $m$ is the mass of MnO$_2$. The $C_s$ value is 209.8 F·g$^{-1}$, close to the value calculated by CV curves at a scan rate of 5 mV·s$^{-1}$, which is more competitive than MnO$_2$ with many other morphologies, such as flowers (168 F·g$^{-1}$),

![Figure 6. Cyclic voltammograms of needle-like, spindle-like, and bulk MnO$_2$ recorded in 1 M Na$_2$SO$_4$ at different scan rates: (a) 5 mV·s$^{-1}$, (b) 100 mV·s$^{-1}$.](image-url)
as-obtained needle-like samples is also examined. It is found that the needle-like MnO₂ supercapacitor retains 75.2% of initial capacitance after 500 cycles, which reveals that cycling does not induce noticeable degradation of the microstructure, and therefore this material is an attractive candidate for supercapacitor electrodes.

4. Conclusions

In summary, MnO₂ with different 1D structures (needles, rods, and spindles) has been fabricated through a facile quick-precipitation procedure just by slightly varying the reaction parameters. By investigation of the mechanism, we speculate that the formations of these unique nanostructures are a spontaneous and preferential process under different reaction conditions. The facile synthetic route and excellent electrochemical behaviors make the obtained needle-like sample a fascinating candidate for supercapacitor electrodes. In fact, the prepared materials are also believed to have applications as catalysts, absorbents, and separation materials and in electromagnetic and electronic devices.

Acknowledgment. The authors are grateful for the financial support of the National Natural Science Foundation of China and China Academy of Engineering Physics (No. BK2009391). and the Natural Science Foundation of Jiangsu province (No. BK2009391).

Supporting Information Available: HRTEM images of the tip of the needle- and rod-like products; TEM images of the intermediates of needle-like products collected at 5, 10, 30, and 60 min; TEM images of the obtained products obtained by using water as the only solvent and adding 50 mL of water; TEM images of as-obtained products when the dropped velocity of the KMnO₄ solution is 0.3 mL·min⁻¹ and 0.5 mL·min⁻¹, and the concentration is 6.6 mg·mL⁻¹; TEM images of as-obtained products when the concentration of KMnO₄ solution is 20 mg·mL⁻¹ and the dropped velocity is 0.1 mL·min⁻¹; yield percentage of as-obtained needle-like products at different aging times. This information is available free of charge via the Internet at http://pubs.acs.org.

References