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Room-temperature synthesis of $\text{MnO}_2 \cdot 3\text{H}_2\text{O}$ ultrathin nanostructures and their morphological transformation to well-dispersed nanorods†

Jinmin Wang, Eugene Khoo, Jan Ma and Pooi See Lee*

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$\text{MnO}_2 \cdot 3\text{H}_2\text{O}$ ultrathin nanostructures with sizes of $\sim 2\text{--}3\text{ nm}$ were synthesized at room temperature and transformation to well-dispersed nanorods was achieved after hydrothermal treatments.

Supercapacitors are devices that combine the advantages of dielectric capacitors, which can deliver high power within a very small period, and rechargeable batteries which can store high energy. They are becoming attractive energy-storage systems particularly for applications in the next generation of high-performance micro-electro-mechanical systems, hybrid vehicles, and portable devices.¹ Pseudocapacitive materials, which support redox reactions at certain potentials, are important for electrochemical energy conversion and storage devices.² Among which, RuO_2 ³ and $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ ⁴ are well-known for their high specific capacitance. Unfortunately, RuO_2 is expensive and may become toxic due to the rare source and possible radioactive impurities. As a result, other metal oxides like MnO_2 nanostructures have attracted considerable interest due to their low cost, high molar density, good chemical resistance and comparable capacitances.⁵

Ultrathin nanostructures⁶ with sizes of less than 10 nm are potentially good candidates for the next generation high-performance supercapacitors because of their greatly enhanced specific surface areas. Several types of ultrathin nanostructures have been synthesized, including Ag, Au, Si, Bi, ZnSe, and CeO_2 .⁷ However, the synthesis of manganese oxide ultrathin nanostructures has not been reported. The redox reactions between oxidative salts of manganese (Mn(VII)) and its reducing salt (Mn(II)) were widely used to synthesize MnO_2 nanostructures, by which only manganese compounds were formed and without undesirable insoluble by-products. MnO_2 nanostructures have been synthesized by mixing the aqueous solutions of KMnO_4 and MnSO_4 ,⁸ or KMnO_4 and Mn(Ac)_2 .^{9,10} However, the obtained MnO_2 nanostructures have large sizes typically in tens to hundreds of nanometres. Ultrathin MnO_2 nanostructures, where at least one dimension is in the ultrathin nanoscale, could create a much larger specific surface area which is very critical in the capacitive process. To achieve this purpose, the synthesis chemistry for MnO_2 nanostructures needs to be further developed. The salts of sulfate and acetate of manganese used in the previously reported redox reaction between Mn(VII) and Mn(II) are non-oxidative; an oxidative salt of Mn(II) should have a distinct effect on the synthesis of MnO_2 nanostructures, which has been proven by

our experiments in this work. To the best of our knowledge, the synthesis of ultrathin MnO_2 nanostructures using KMnO_4 and another oxidative manganese salt has not been reported before.

Herein, we demonstrate the room-temperature synthesis of $\text{MnO}_2 \cdot 3\text{H}_2\text{O}$ ultrathin nanostructures by using KMnO_4 and $\text{Mn(NO}_3)_2$ in which NO_3^- ions act as an additional kind of oxidative species besides MnO_4^- ions. Subsequently, well-dispersed nanorods were successfully obtained by hydrothermal treatments of the $\text{MnO}_2 \cdot 3\text{H}_2\text{O}$ ultrathin nanostructures.

The relationship between phase formation and hydrothermal conditions (temperatures and time) was investigated by comparing the X-ray diffraction (XRD) patterns (shown in Fig. 1) of the products synthesized at different temperatures and time. The XRD peaks of the products synthesized at room temperature (Fig. 1a) and 100 °C (Fig. 1b) can be well indexed to tetragonal $\alpha\text{-MnO}_2 \cdot 3\text{H}_2\text{O}$ (JCPDS 44-0140). In fact, the XRD peaks of $\alpha\text{-MnO}_2 \cdot 3\text{H}_2\text{O}$ (JCPDS 44-0140) and $\alpha\text{-MnO}_2$ (JCPDS 44-0141) are too similar to be well-distinguished easily. Therefore, thermogravimetric analyzer (TGA) is necessary to check on the presence of hydrates. There is a significant weight loss reflected from the TGA analysis of the room-temperature synthesized product (See Fig. S1 in ESI†), which implies that the product contains hydrates; confirming the hydrated compound (instead of anhydrous compound). It should be noted that one clear broad peak and a weak peak at 2θ angles of $\sim 36.7^\circ$ and $\sim 65.4^\circ$ are detected from the XRD pattern (Fig. 1a) of the product synthesized at room temperature. The broadened XRD peaks are common for nanocrystals, indicating a small crystalline particle size. When the hydrothermal temperature is increased to 120 °C, a small XRD peak (labeled with a star) occurs at a 2θ angle of 22.4° (Fig. 1c) and becomes stronger at 150 °C (Fig. 1d), which implies that a new phase is generated at higher temperatures. This new phase can be identified as $\gamma\text{-MnO}_2$ (JCPDS 65-1298). After a 24 h hydrothermal treatment, the product fully transforms into $\gamma\text{-MnO}_2$. This compositional change arising from the decomposition of hydrated manganese oxide is sluggish under hydrothermal conditions. The decomposition of $\alpha\text{-MnO}_2 \cdot 3\text{H}_2\text{O}$ takes place when the reaction temperature exceeds the transition temperature of the hydrated nanostructures which is expected to be lower than that of the bulk material.

Besides the hydrothermal temperatures, the amount of KMnO_4 was found to be another controlling parameter of the resultant composition in the hydrothermal products. At small amounts (9.2, 13.0, 15.0, 17.0 mL) of 0.1 M KMnO_4 , the dominant phase of the hydrothermal products synthesized at 150 °C for 6 h is $\gamma\text{-MnO}_2$ (Fig. 2a–d), with the presence of pure $\gamma\text{-MnO}_2$ at 9.2 mL of KMnO_4 . However, the dominant phase is $\alpha\text{-MnO}_2 \cdot 3\text{H}_2\text{O}$ at larger amounts (20.0, 25.0 mL) of

School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore. E-mail: pslee@ntu.edu.sg; Tel: +65-67906661

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Fig. 1 XRD patterns of (a) room-temperature synthesized α - $\text{MnO}_2 \cdot 3\text{H}_2\text{O}$ ultrathin nanostructures, hydrothermal products synthesized with 13.8 mL of 0.1 M $\text{Mn}(\text{NO}_3)_2$ and 20.0 mL of 0.1 M KMnO_4 at (b) 100, (c) 120, (d) 150 °C for 6 h and (e) at 150 °C for 24 h.

0.1 M KMnO_4 (Fig. 1a–d and Fig. 2e). It must be noted that the XRD peaks of (101) planes of γ - MnO_2 become weaker and the intensities of the (110), (200) planes of α - $\text{MnO}_2 \cdot 3\text{H}_2\text{O}$ are stronger with increasing amounts of KMnO_4 . This clearly shows that the γ - MnO_2 phase is stable at small amounts of KMnO_4 whereas α - $\text{MnO}_2 \cdot 3\text{H}_2\text{O}$ is more stable at larger amounts of KMnO_4 . This is related to the large driving force (fast reaction rate) at larger amounts of KMnO_4 to form an α -polymorph consisting of double chains of $[\text{MnO}_6]$ octahedra forming $[2 \times 2]$ tunnels in the presence of more K^+ ions and water molecules.¹¹

The morphology of the room-temperature synthesized product is shown in Fig. 3. The product looks like nanoscaled spheres from the field emission scanning electron microscopy (FESEM) and low-magnification transmission electron microscopy (TEM) images (Fig. 3a and b). It is found that the spheres consist of many fine nanostructures from the higher-magnification TEM images (Fig. 3c and d). The nanostructures have typical sizes of ~ 2 –3 nm, therefore the nanostructures and their assembled spheres are called ultrathin nanostructures and hierarchical nanostructures, respectively. To the best of our knowledge, this is the first report on the synthesis of α - $\text{MnO}_2 \cdot 3\text{H}_2\text{O}$ ultrathin nanostructures. This morphology is different from the plate-like structures¹⁰ previously reported using non-oxidative salt of manganese.

Fig. 2 XRD patterns of the hydrothermal products synthesized at 150 °C for 6 h with 13.8 mL of 0.1 M $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ and different amounts of 0.1 M KMnO_4 : (a) 9.2 mL, (b) 13.0, (c) 15.0, (d) 17.0 and (e) 25.0 mL.

Fig. 3 (a) FESEM, (b)–(d) TEM, (e) HRTEM images and (f) EDS spectrum of α - $\text{MnO}_2 \cdot 3\text{H}_2\text{O}$ ultrathin nanostructures.

Furthermore, their compositions are also different: the as-synthesized ultrathin nanostructures are α - $\text{MnO}_2 \cdot 3\text{H}_2\text{O}$ whereas the previously reported plate-like structures are MnO_2 .^{8b,10} It shows that the morphology and composition of the products can be changed by employing an oxidative salt (nitrate) of manganese. A high-resolution TEM (HRTEM) image of the ultrathin nanostructures is shown in Fig. 3e. The crystal lattice can be seen, indicating the crystalline structure of the as-synthesized ultrathin nanostructures. The lattice spacing of 0.34 nm corresponds to the plane distance of (220) planes in α - $\text{MnO}_2 \cdot 3\text{H}_2\text{O}$, which shows that the growth direction of the ultrathin nanostructures is almost along [220] direction. Fig. 3f shows the energy dispersive spectroscopy (EDS) spectrum of the ultrathin nanostructures, in which strong peaks of Mn and O can be found. A small amount of Na and K found in the spectrum should arise from the reactants which were not completely removed by washing.

Plate-like nanostructures with large sizes were synthesized using KMnO_4 and MnSO_4 ,^{8b,10} whereas, in our work, α - $\text{MnO}_2 \cdot 3\text{H}_2\text{O}$ ultrathin nanostructures were formed and assembled into sphere-like hierarchical nanostructures. The reason for such remarkable differences can be revealed by analyzing the redox reaction between KMnO_4 and $\text{Mn}(\text{NO}_3)_2$ solutions. It is well-known that MnO_4^- is a very strong oxidant, and Mn^{2+} can be regarded as a reducing agent, so the reaction is a typical redox reaction, which can be expressed in the following:

It is believed that NO_3^- ions played a critical role in the formation of α - $\text{MnO}_2 \cdot 3\text{H}_2\text{O}$ ultrathin nanostructures. It must be noted that the individual aqueous solutions of the reactants are both acidic because MnO_4^- and Mn^{2+} ions are stable in acidic media. In fact, the pH of the solution was found to be ~ 1.2 after the reaction. It implies that the reaction was carried out in a strong acidic medium, in which HNO_3 served as an additional oxidant in addition to KMnO_4 . The half-cell reactions of $\text{MnO}_4^-/\text{MnO}_2$ and $\text{NO}_3^-/\text{NO}_2$ are:

Fig. 4 FESEM images of hydrothermal products synthesized with 13.8 mL of 0.1 M $\text{Mn}(\text{NO}_3)_2$ and 20.0 mL of 0.1 M KMnO_4 at (a) 100, (b) 120, (c) 150 °C for 6 h, (d) 150 °C for 24 h, (e) with 13.8 mL of 0.1 M $\text{Mn}(\text{NO}_3)_2$ and 25.0 mL of 0.1 M KMnO_4 at 150 °C for 6 h, and (f) HRTEM image of a single typical nanorod.

The Nernst equation,

$$E = E^\theta + (RT/zF)\ln[\text{Ox}]/[\text{Red}] \quad (4)$$

so the potentials of $\text{MnO}_4^-/\text{MnO}_2$ and $\text{NO}_3^-/\text{NO}_2$ are

$$E_{\text{MnO}_4^-/\text{MnO}_2} = E^\theta + (RT/3F)\ln[\text{MnO}_4^-][\text{H}^+]^4 \quad (5)$$

and

$$E_{\text{NO}_3^-/\text{NO}_2} = E^\theta + (RT/F)\ln[\text{NO}_3^-][\text{H}^+]^2/(p_{\text{NO}_2}/100) \quad (6)$$

where E is the half-cell oxidation potential, E^θ is the standard half-cell oxidation potential, R is the universal gas constant, T is the absolute temperature, F is the Faraday constant, z is the number of electrons transferred in the cell reaction or half-reaction, p is the pressure with the unit of kPa.

Eqn (5) and (6) show that both of the oxidizing abilities of MnO_4^- and NO_3^- ions are markedly enhanced with the increase of H^+ ions concentration. Thus, Mn^{2+} ions will be more easily oxidized to MnO_2 (in the form of $\text{MnO}_2 \cdot 3\text{H}_2\text{O}$), which increases the reaction rate and results in a large supersaturation of the nucleation. As a result, small nuclei of $\text{MnO}_2 \cdot 3\text{H}_2\text{O}$ were quickly formed and the subsequent nuclei growth was restrained due to the exhaustion of the reactants. The small nuclei have large specific surface area and high surface energy which provide a driving force for their aggregation to reduce the surface areas. Finally, the nuclei grew into ultrathin nanostructures and assembled into larger hierarchical structures.

The FESEM images of the products after hydrothermal treatments show different morphologies from the room-temperature synthesized hierarchical nanostructures. Straight $\alpha\text{-MnO}_2 \cdot 3\text{H}_2\text{O}$ nanorods with diameters of $\sim 10\text{--}20$ nm and lengths of ~ 500 nm were obtained by simple hydrothermal treatments (Fig. 4a–c, e). Even at the boiling point of water, $\alpha\text{-MnO}_2 \cdot 3\text{H}_2\text{O}$ nanorods can be formed, though the product contains some irregular nanoparticles, which shows that a hydrothermal treatment facilitates the formation of well-crystallized nanorods. With the increase in reaction temperature, more irregular particles were obtained. According to the XRD patterns of the products, the irregular particles should have a different composition from the dominant presence of nanorods in the products. It can be confirmed by comparing the FESEM

images of the product synthesized for a long time (24 h) in which only nanoparticles were observed (Fig. 4d). The corresponding XRD pattern indicates only $\gamma\text{-MnO}_2$ (Fig. 1e) can be indexed. Therefore, the results show that the composition can be changed by tailoring the hydrothermal time. The typical HRTEM image of a single nanorod is shown in Fig. 4f. The clear crystal lattice shows that the nanorod is single-crystalline. The lattice spacing of 0.25 nm corresponds to the distance of (400) planes of $\alpha\text{-MnO}_2 \cdot 3\text{H}_2\text{O}$. The growth direction of the nanorods is almost along the [400] direction.

In conclusion, $\alpha\text{-MnO}_2 \cdot 3\text{H}_2\text{O}$ ultrathin nanostructures with sizes of $\sim 2\text{--}3$ nm were successfully synthesized at room temperature, which is attributed to the employment of additional oxidant (nitrate) in addition to KMnO_4 . The oxidizing abilities of MnO_4^- and NO_3^- ions are markedly enhanced in an acidic medium. Well-dispersed nanostructures can be obtained by a simple hydrothermal treatment of the ultrathin nanostructures at a quite low hydrothermal temperature (100 °C). It was found that the composition and phase of the hydrothermal product can be tuned by hydrothermal temperature, time and amount of KMnO_4 . $\gamma\text{-MnO}_2$ phase starts to form by a hydrothermal treatment at 120 °C for 6 h, its proportion increases at 150 °C for 6 h, and it becomes pure $\gamma\text{-MnO}_2$ at 150 °C for 24 h. With the composition changes, the morphologies of the hydrothermal products evolve into $\gamma\text{-MnO}_2$ nanoparticles from $\alpha\text{-MnO}_2 \cdot 3\text{H}_2\text{O}$ nanorods. $\gamma\text{-MnO}_2$ is stable with the use of a small amount of KMnO_4 whereas $\alpha\text{-MnO}_2 \cdot 3\text{H}_2\text{O}$ is more stable with a large amount of KMnO_4 under hydrothermal conditions.

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