

系列纳米结构锰氧化物的水热合成

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摘要: 以 KMnO_4 为锰源、抗坏血酸(AA)为还原剂, 采用水热法制备系列纳米结构锰氧化物。通过调节反应物的物质的量的比、水溶液的 pH 值、反应温度和反应时间, 制备出了不同纳米结构的锰氧化物, 包括 Mn_3O_4 纳米粒子、 MnOOH 、 $\alpha\text{-MnO}_2$ 和 $\beta\text{-MnO}_2$ 纳米棒。采用 XRD 和 TEM 测试技术对合成产物进行了表征, 同时对其反应机理进行了探讨。

关键词: 水热法; 纳米结构锰氧化物; 氧化还原反应; 机理

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Synthesis of Various Nanostructured Manganese Oxides via Facile Hydrothermal Reaction

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Abstract: A versatile hydrothermal reaction between KMnO_4 and ascorbic acid(AA) was developed to synthesize manganese compounds. A variety of nanostructured manganese oxides including Mn_3O_4 nanoparticles, MnOOH , $\alpha\text{-MnO}_2$ and $\beta\text{-MnO}_2$ nanorods have been prepared through adjusting the molar ratio of the reactants, pH value of the aqueous solution, reaction temperature and reaction time. The products were characterized by X-ray powder diffraction(XRD) and transmission electron microscopy(TEM). The possible reaction mechanism was discussed.

Key words: Hydrothermal method; nanostructured manganese oxides; redox reaction; mechanism

Transitional metal manganese element can exist in various oxidation states ranging from +2 to +7, and gives to a rather complex oxides system, with the most usual stoichiometrics MnO , Mn_3O_4 , Mn_2O_3 , MnOOH (oxyhydroxide) and MnO_2 . Moreover, these manganese oxides have polymorphic forms. It has been found that manganese oxides are of considerable importance in technological applications including ion-exchange, molecular adsorption, catalysis, as well as electrochemical and magnetic uses, due to their outstanding structural flexibility combined with novel chemical and physical properties^[1-4]. For instances, polymorphs of

MnO_2 ^[3,4] and Mn_3O_4 ^[5] have been proposed as cheap, environment-friendly catalysts for the combustion of volatile organic compounds(VOCs), the total oxidation of CH_4 and CO ^[5,6] and the selective reduction of nitrobenzene^[7-9]. Mn_3O_4 also possesses interesting magnetic^[10,11] and electrochemical properties^[12-14]. Among manganese oxides, MnOOH , $\alpha\text{-}$, $\beta\text{-}$ and $\gamma\text{-MnO}_2$ present particular interests because of their applications as catalysts and as electrode materials in lithium batteries^[15-17]. Nanostructured MnOOH has been proven to be good precursor to synthesize nanostructured Li-Mn-spinel and other manganese oxides such as MnO_2 , Mn_2O_3 and Mn_3O_4 ^[18-20].

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Recently, manganese oxides with various nanostructures, particularly with one-dimensional nanostructures have attracted much attention^[21-24], because their performance in many fields including separation, chemical sensing devices, biology and electronics could be potentially enhanced through processing their nanostructures with well-controlled composition, dimension and morphology. Although much effort has been made^[23,25,26], the synthesis of nanomaterials with controllable phase, shape and size continues to be a major challenge in nanoscience and nanotechnology. To face this challenge, different strategies and even sophisticated synthesis procedures are usually pursued. On the other hand, much of the motivation for chemistry and material scientists is dedicated to developing simple routes to nanomaterial synthesis.

Here, we report a simple and versatile approach to the synthesis of a variety of manganese compounds including $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, MnCO_3 , Mn_3O_4 , MnOOH , $\alpha\text{-MnO}_2$ and $\beta\text{-MnO}_2$ just via a simple hydrothermal reaction. This versatile hydrothermal method is based on the redox reaction between KMnO_4 and ascorbic acid (AA) and can provide a successful control over the chemical composition, phase purity and morphology of the manganese oxides simply through adjusting the molar ratio of the reactants, pH value of the aqueous solution, reaction temperature and reaction time. The virtues of this method lie not only in the synthesis of various manganese compounds but also in the successful preparation of nanostructured manganese oxides. It is worth noting that the obtained Mn_3O_4 sample exists in well-dispersed nanocubes of 20~40 nm, and MnOOH , $\alpha\text{-MnO}_2$ and $\beta\text{-MnO}_2$ samples have nanorod morphology. The facile and large-scale fabrication of nanostructured manganese oxides is of fundamental importance for their practical and potential applications.

1 Experimental

The reagents KMnO_4 and ascorbic acid(AA) were of analytical grade from Shanghai Chemicals Company and were used without further purification. An appropriate amount of KMnO_4 and AA was put in a

stainless autoclave of about 50 mL capacity, then 30 mL of distilled water was added. To prepare different manganese compounds, the molar ratio of KMnO_4 and AA was tuned in the range of 1:2 to 5:1, the pH values of the solution were adjusted through adding sulphuric acid and sodium hydroxide, respectively, the reaction temperature was changed in the range of 80~170 °C and the reaction time was varied from 12 to 48 h. Detailed synthesis conditions are listed in Table 1. The autoclave was sealed and maintained at a given temperature for a fixed time, then cooled to room temperature naturally. The resulted solid products were filtered and washed with distilled water and ethanol three times, respectively to remove possible residual ions in the final products, and finally dried at 70 °C for 4 h. The obtained samples were collected for characterization.

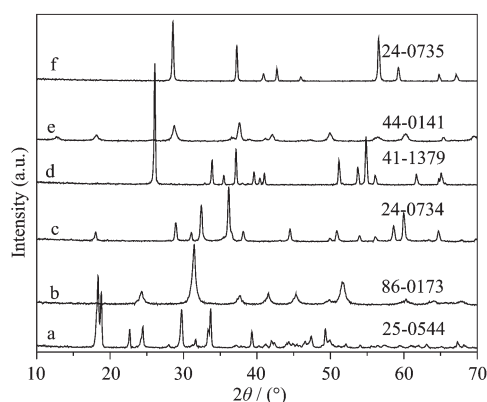
The as-prepared samples were characterized by X-ray powder diffraction(XRD) on a Rigaku D/max-rB X-ray diffractometer with a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.154\,178\text{ nm}$) operated at 40 kV and 80 mA, and the scan rate (2θ) of $8^\circ \cdot \text{min}^{-1}$ was applied to record the pattern in the 2θ range of $10^\circ \sim 70^\circ$ by means of a solid detector and a scintillation counter. Transmission electron microscopic(TEM) images and electron diffraction (ED) patterns were taken with Hitachi H-800 at an accelerating voltage of 200 kV.

2 Results and discussion

This hydrothermal reaction is based on a redox reaction, with KMnO_4 as the oxidizing agent and AA as the reducing agent. Through the adjustment of such experiment parameters as the molar ratio of KMnO_4 and AA, pH value of the aqueous solution, reaction temperature and reaction time, various manganese compounds can be obtained(see Table 1). The phase purity of the products was examined by XRD measurement. Fig.1 shows the XRD patterns of the as-prepared manganese compounds. The XRD patterns from Fig.1a to 1f can be indexed to $\alpha\text{-MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, MnCO_3 , Mn_3O_4 , MnOOH , $\alpha\text{-MnO}_2$ and $\beta\text{-MnO}_2$, respectively. The referred PDF card numbers have been marked correspondingly in Fig.1.

Table 1 Obtained products and their corresponding reaction parameters

Sample	Product	Molar ratio (KMnO ₄ :AA)	Temperature / °C	Time / h	pH value (initial solution)
1	α -MnC ₂ O ₄ ·2H ₂ O	1:2	80~120	24	About 3 (original pH value of the solution)
2	MnCO ₃	1:1	150~170	48	10
3	Mn ₃ O ₄	3:1	120	48	11
4	MnOOH	4:1	100	24	2
5	α -MnO ₂	5:1	90~160	24	0.5 mol·L ⁻¹ H ₂ SO ₄
6	β -MnO ₂	5:1	170	24	0.5 mol·L ⁻¹ H ₂ SO ₄



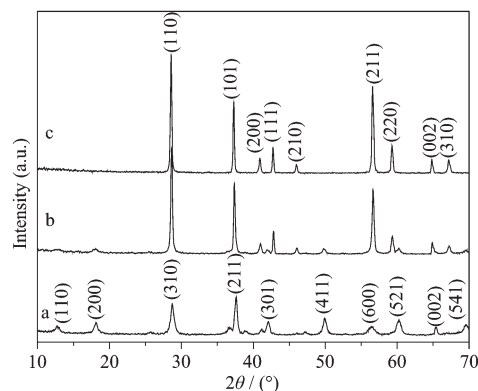
(a) α -MnC₂O₄·2H₂O; (b) MnCO₃; (c) Mn₃O₄; (d) MnOOH;
(e) α -MnO₂; (f) β -MnO₂

Fig.1 XRD patterns of the samples obtained under different reaction conditions

Table 1 lists the obtained products and their corresponding reaction parameters. It seems that the interrelation between products and the reaction parameters is not easy to be expounded, because the final products are comprehensively controlled by these parameters. As a matter of fact, this versatile hydrothermal reaction is intrinsically governed by the oxidizing ability of the solution. From MnC₂O₄·2H₂O and MnCO₃ to Mn₃O₄, to MnOOH and to MnO₂, the valence state of manganese changes increasingly from Mn²⁺ to Mn⁴⁺, and accordingly the oxidizing ability of the reaction system should have been increased through adjusting the reaction parameters. The results reveal that the molar ratio of KMnO₄ and AA, pH value of the solution and reaction temperature are the key factors affecting the phase of products, which will be explained qualitatively in the section of the formation mechanism for the manganese compounds. From Table 1, it can be seen that the Mn²⁺ compounds MnC₂O₄·2H₂O and MnCO₃ can be obtained at lower

molar ratio of KMnO₄ to AA. However, for the synthesis of MnCO₃, the pH value of the reaction solution is adjusted to base condition which is beneficial for the stable existence of MnCO₃. Besides, the synthesis of MnCO₃ needs a higher reaction temperature than that of MnC₂O₄·2H₂O. Experiments show that CO₃²⁻ is a deeper oxidation state of AA, compared with C₂O₄²⁻. In Table 1, it can also be found that with the increasing molar ratio of KMnO₄ to AA from 3:1 to 4:1 and 5:1, Mn₃O₄, MnOOH and MnO₂ can be obtained, respectively.

α -MnO₂ and β -MnO₂ are different in that the α -type is constructed from double chains of [MnO₆] octahedra forming 2×2 tunnels, while the β -type is composed of single chains of [MnO₆] octahedral with 1×1 tunnels. In our experiments, the crystallographic structure difference of α -MnO₂ and β -MnO₂ can be controlled simply by the reaction temperature, which has been confirmed by the XRD analysis. The XRD patterns in Fig.2 clearly indicate the evolution of the



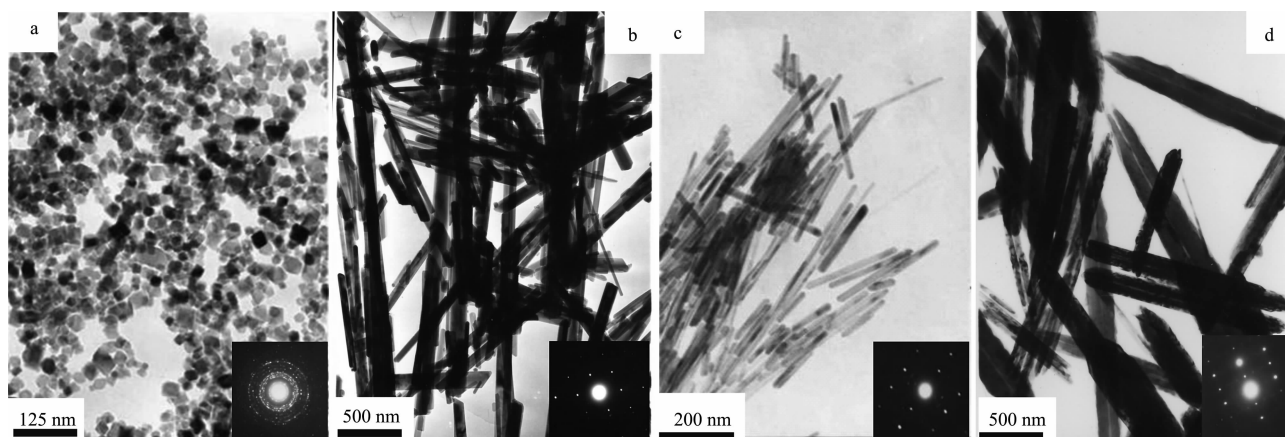
(a) α -MnO₂(160 °C, 12 h); (b) the intermediate (170 °C, 12 h);
(c) β -MnO₂(170 °C, 24 h)

Fig.2 XRD patterns of MnO₂ prepared at different temperature and time

MnO₂ structural forms from α -type to β -type with the reaction temperature. It can be seen that α -MnO₂ is stable at lower temperature, while β -MnO₂ exists at higher temperature. α -MnO₂ changes into β -MnO₂ at 170 °C under the mentioned conditions. The latter was reported to be the most thermodynamically stable phase of manganese dioxide^[26].

The nanostructures of the as-synthesized manganese oxides(including oxyhydroxide) were observed with TEM. Fig.3 displays the TEM images of the as-synthesized manganese oxides. Fig.3a shows the morphology of the obtained Mn₃O₄ powder. It exists in well-dispersed nanocubes with the edge length ranging from 20 to 40 nm. The inset in Fig.3a is the

corresponding electron diffraction (ED) pattern of the Mn₃O₄ powder. It indicates that the sample is composed of many tiny Mn₃O₄ nanocrystals. The morphology of MnOOH is shown in Fig.3b. It consists of nanorods with diameters of 40~100 nm and lengths of 0.5~2 μ m. Fig.3c shows the morphology of α -MnO₂, which is composed of nanarods with diameters of 10~20 nm and lengths of 100~500 nm. The image of β -MnO₂ shown in Fig.3d is also composed of nanorods with diameters of 100~500 nm and lengths of 0.5~3 μ m. The insets in Fig.3b, 3c and 3d are the corresponding ED patterns of MnOOH, α -MnO₂ and β -MnO₂ nanorods, which are taken from single rods, indicating that they are single crystalline.

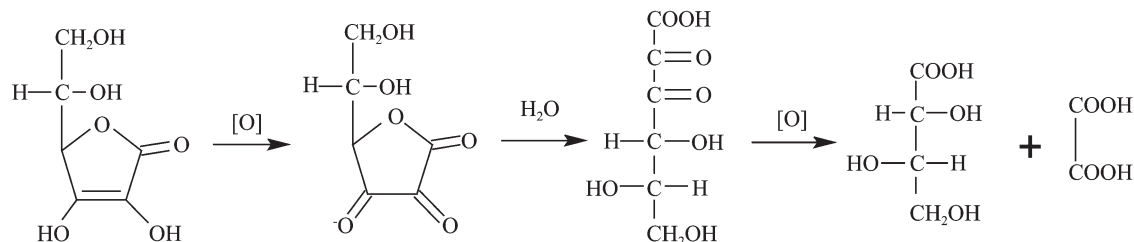


(a) Mn₃O₄; (b) MnOOH; (c) α -MnO₂; (d) β -MnO₂

Fig.3 TEM images of the as-prepared manganese oxides

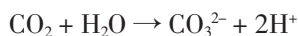
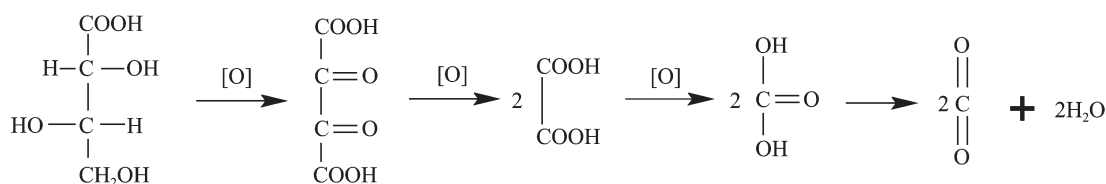
Based on our experimental results, the formation mechanism of the various manganese compounds can be suggested. Ascorbic acid(also called vitamin C) is a biological reducing agent and is easily oxidized. Under the hydrothermal conditions, with KMnO₄ as oxidizing agent, ascorbic acid is first oxidized into dehydroa-

scorbic acid(DHA). DHA is then hydrolyzed into 2,3-diketogulonic acid in the aqueous solution and 2,3-diketogulonic acid is further oxidized into threonic acid and oxalate. This oxidation-decomposition process is also the one of vitamin C undergoing in human body. It can be expressed in the following chemical equations



When oxidizing ability is increased the threonic acid can be deeply oxidized into CO₂, which is then

hydrolyzed into CO₃²⁻. This process may be expressed in the following chemical equations



Meanwhile, the Mn^{7+} in KMnO_4 is reduced into Mn^{2+} , which would combine with $\text{C}_2\text{O}_4^{2-}$ or CO_3^{2-} in the aqueous solution to produce $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ or MnCO_3 . As long as the oxidizing atmosphere is properly controlled, the products $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and MnCO_3 can be obtained, respectively.

If the amount of KMnO_4 is in excess in the system, i.e. the molar ratio of KMnO_4 and AA is greater than 1, the remaining Mn^{7+} will react with Mn^{2+} to yield manganese oxides with a middle valence state. The existence of the middle valence state of Mn in the manganese oxides depends on the oxidizing ability of the solution. Taking an acid solution as an example, there exists the following equation



According to Nernst equation, the potential E is given by

$$E = E^\ominus - \frac{RT}{nF} \ln \frac{c_{\text{Mn}^{2+}}}{c_{\text{MnO}_4^-} c_{\text{H}^+}^8}$$

It can be rearranged as

$$E = E^\ominus - \frac{RT}{nF} \ln c_{\text{Mn}^{2+}} + \frac{RT}{nF} \ln c_{\text{MnO}_4^-} + 8 \times \frac{RT}{nF} \ln c_{\text{H}^+}$$

Where the standard potential $E^\ominus = 1.51 \text{ V}$. This equation enables us to calculate the potential E . Here we just make a qualitative analysis. It can be seen that the potential E increases as the concentrations of H^+ and/or MnO_4^- are increased. In other words, the oxidizing ability of the solution will be enhanced with the increasing of c_{H^+} and $c_{\text{MnO}_4^-}$. Moreover, the influence of c_{H^+} is more significant than that of $c_{\text{MnO}_4^-}$, because its effect is enhanced by 8 times according to the above equation. Therefore, to produce manganese oxides with higher oxidation states, higher acidity and greater molar ratio of KMnO_4 to AA is beneficial, which is in agreement with our experiment results. In addition to the major effect of the molar ratio of KMnO_4 to AA and pH value of the solution, reaction temperature and time also

have influences on the products. For example, we also synthesized MnOOH nanorods under basic condition ($0.02 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution) with a reaction temperature of 175°C and time of one week. In the phase conversion of $\alpha\text{-MnO}_2$ into $\beta\text{-MnO}_2$, reaction temperature plays a significant role.

3 Conclusion

In summary, a facile hydrothermal reaction between KMnO_4 and ascorbic acid (AA) was developed to produce various manganese compounds including several nanostructured manganese oxides. Well-dispersed Mn_3O_4 nanocubes of $20\sim 40 \text{ nm}$, MnOOH nanorods with diameters of $40\sim 100 \text{ nm}$, $\alpha\text{-MnO}_2$ nanorods with diameters of $10\sim 20 \text{ nm}$ and $\beta\text{-MnO}_2$ nanorods with diameters of $100\sim 500 \text{ nm}$ were obtained, respectively, through tuning the molar ratio of KMnO_4 to AA, pH value of the solution, reaction temperature and time. The reaction mechanism can be well explained according to Nernst equation.

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