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Synthesis, Characterization and Morphology Controlling Investigation of Hexagonal Prism Molybdenum Trioxide

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Abstract: Molybdenum trioxide with different morphologies was synthesized by hydrothermal synthesis method using ammonium heptamolybdate tetrahydrate (AHM) as the precursor. The effects of the reaction temperature, reaction time and the addition amount of nitric acid were investigated. Simultaneously, the effects of the fresh reaction solution and the aged solution on the morphology of the products were also studied. The experiment results showed that fresh reaction solution crystallizing at 180 °C for 40 h could produce uniform and regular hexagonal prism of MoO₃. However, when the reaction solution was aged for a long time the MoO₃ obtained was sheet form. Finally, the effect of inorganic salts on the morphology of hexagonal molybdenum oxide has also been investigated. The salts including FeCl₃, Fe(NO₃)₃, and Ce(NO₃)₃ inhibited the formation of regular hexagonal MoO₃ except KBr which decreased the diameter of section for hexagonal MoO₃ product. The samples were characterized via field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and Fourier transformation infrared spectroscopy (FT-IR).

Key words: Hydrothermal synthesis; MoO₃; Morphology; Characterization

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Dimensionality is important in determining the characteristics of nanomaterials. Over the past few years, since the discovery of carbon nanotubes, much effort has been devoted to the synthesis of one-dimensional (1D) nanowires^[1], nanorods^[2,3], and nanobelts^[4], due to the importance of fabricating nanodevices and nanosensors. The layered transition metal oxides and chalcogenides are very important anisotropic materials, of which V₂O₅, WO₃, MoO₃, MoS₂ and WS₂ have been extensively investigated owing to their extensively technological applications. For example, MoO₃ and its derivatives have been known for their widely used in industry as catalysts, e. g. in alcohol oxidation. Tatibou t et al.^[5], used oriented MoO₃ crystallites to study the structure sensitivity of the ethanol oxidation, and Iwasawa et al.^[6], Ono et al.^[7] and

Zhang et al.^[8] used supported samples to study molybdate-support interactions. On the basis of studies of structure^[5], reactivity, infrared spectroscopy (IR), extended X-ray adsorption fine structure spectroscopy (EXAFS), and Raman spectroscopy (LRS)^[6,7], various authors have concluded that Mo = O bonds are the active sites for acetaldehyde formation. Mo dimers were suggested to be present by Iwasawa et al.^[6,9,10] on MoO₃/SiO₂ prepared from organometallic precursors. The catalysts with Mo dimer structure on the surface showed very high activity and selectivity to acetaldehyde^[6,9,10]. Moreover, MoO₃ also have promising applications in building display devices, sensors, smart windows, lubricants, battery electrodes, and nanostructured materials in the latest context^[11-17].

Usually, MoO₃ has been prepared into various

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morphologies using host materials and templates^[2,18]. MoO_3 nanofibers with diameters of 50 ~ 150 nm and lengths up to 15 μm have been prepared via hydrothermal process, with the precursor of molybdic acid $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ and the template of amines $\text{C}_n\text{H}_{2n+1}\text{NH}_2$ ^[19]. Hollow MoO_3 nanospheres have also been synthesized from the precursor compound $\text{MoO}_2(\text{OH})(\text{OOH})$ with a triblock copolymer method^[20]. Moreover, many other molybdenum trioxide with different morphologies (nanorods, nanotubes, and mesostructured toroids) are now fabricated based on different procedures and synthesis techniques.

Although there are many synthesis methods used for preparing 1D nanostructured anisotropic molybdenum trioxide, the hexagonal prism-like MoO_3 has not been investigated in detail, including a series of influence factors, such as reaction time, reaction temperature and the pH values et al. . In this contribution, we studied the influence of the above conditions on the morphology, and also the effects of the addition of inorganic salts on the products morphology were studied.

1 Experiment

In a typical procedure, 10 mL of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ saturated solution was acidified (pH = 5) using 2.2 mol L^{-1} nitric acid. Then it was diluted with 10 mL deionized water, and further acidified using the same

concentration nitric acid and stirred for 30 min. The resultant solution, together with white precipitate, was transferred into a Teflon-lined stainless steel autoclave and heated at 180 C for 40 h. The final product was filtered and washed with water, ethanol and ether, followed by drying at room temperature.

When the effect of inorganic salts was investigated, the synthesis procedure was the same to the above except that 20 mL of inorganic salt solutions, with the concentration of 0.5 mol L^{-1} , were added to the pH = 5 AHM solution.

FE-SEM image was recorded with a JSM-6701F field emission scanning electron microscopy. XRD characterization was performed on a Rigaku D/Max-3B diffractometer with Cu $\text{K}\alpha$ radiation (scanning rate = 4°/min, voltage = 40 kV, current = 25 mA). Fourier transformation infrared spectroscopy (FT-IR) was carried out with a Thermo Nicolet 5700 FT-IR Spectrometer.

2 Results and discussion

2.1 The effect of the crystallization temperature

The effect of the crystallization temperature on the as-prepared MoO_3 samples was carried out at 120 °C, 150 °C, 180 °C and 200 °C, respectively, while the reaction time was fixed at 40 h (Fig. 1). At 120 °C, a hexagonal crystal rudiment appeared, and the crystalli-

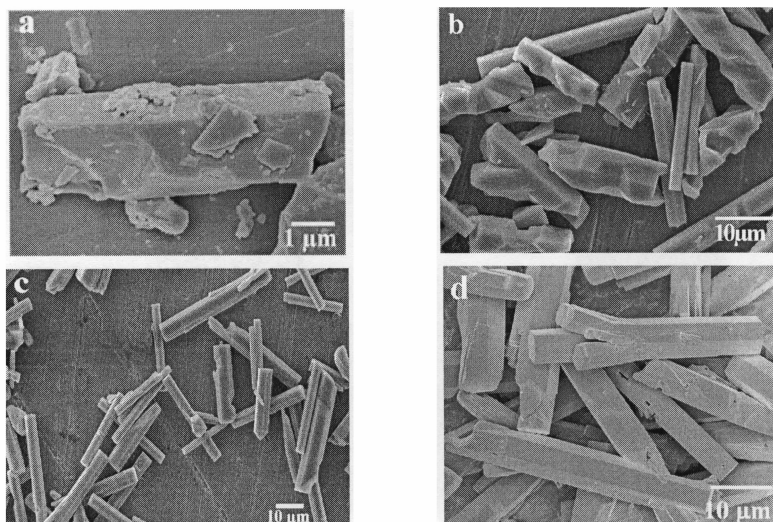


Fig. 1 FE-SEM images of as-prepared MoO_3 samples with constant reaction time and different temperatures (a) 120 °C; (b) 150 °C; (c) 180 °C and (d) 200 °C

zation was incomplete. When the temperature was up to 150 °C although the crystallization process was further promoted, the coarse and defective crystal was still irregular. It could be seen that the regular and uniform hexagonal prism of MoO₃, of which the diameter of section was approximately 3 μm and the length was around 15 μm, was obtained at 180 °C. Further increasing the reaction temperature up to 200 °C some small crystal branches outgrew on the surface. It was

demonstrated that below 200 °C the increasing of the temperature was advantageous to product crystallization, but higher temperature than 180 °C would cause the crystal branches to appear.

2.2 The effect of the crystallization time

The crystallization temperature was fixed at 180 °C while the crystallization time was varied in the range of 9 ~ 60 h. From the FE-SEM images of Fig. 2, it was clearly showed that the growth of MoO₃ highly depended

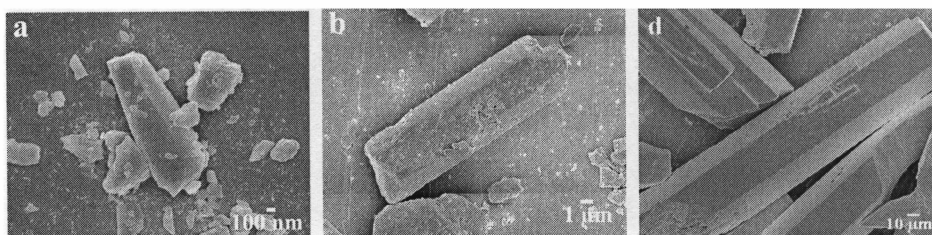


Fig. 2 FE-SEM images of as-prepared MoO₃ samples with constant reaction temperature but with different reaction time (a) 9 h; (b) 24 h; (c) 40 h (Fig. 1c) and (d) 60 h

on the reaction time. When the reaction time was shorter than 40 h, the crystallization was incompleting and the clear-cut hexagon was absent. However, small branches appeared in the hexagonal surface when the reaction time was longer than 40 h. Such phenomenon was also observed when the temperature was higher than 180 °C with the constant reaction time. From the comparison of the product images, it was sure that the perfect crystal could be obtained at 40 h, shorter or longer reaction times were both disadvantageous for the crystal growth.

2.3 The effect of pH values

To convert molybdate anions of Mo₇O₂₄⁶⁻ to neutral MoO₃, excess divalent oxygen anions must be re-

moved. Stoichiometrically, three divalent oxygen anions per Mo₇O₂₄⁶⁻ must be combined with protons from the acidic medium:



In the above equilibrium, the reaction would shift to the right with high concentrations of both Mo₇O₂₄⁶⁻ and H⁺. It is thus anticipated that the formation of MoO₃ should have a strong dependence on the acid concentration (protons provided). The pH values of the reaction system with different addition amount of HNO₃ were shown in Table 1, and the corresponding FE-SEM images were shown in Figure 3. The images in Figure 3 illustrated that the crystallization was partial

Table 1 The pH values after reaction corresponding to different addition amount of HNO₃

Sample	AHM saturated solution (mL)	HNO ₃ (mL)	Temperature (°C)	Time (h)	pH (after reaction)
1	10	5	180	40	1.02
2	10	10	180	40	0.20
3	10	15	180	40	0

and the diameter of section of the product was big when the addition volume of HNO₃ was 5 mL. However, the perfect and complete morphology was obtained with 10 mL of HNO₃. When the addition amount of HNO₃ was increased to 15 mL the complete crystal could also be obtained. Nevertheless, the surface of the product be-

came rough. In a word, the results were suggested that the pH value would take significant effect on the morphology of the product.

2.4 The effect of the aged time for the acidified AHM precursor solutions

Figure 4 shows the FE-SEM images of as-prepared

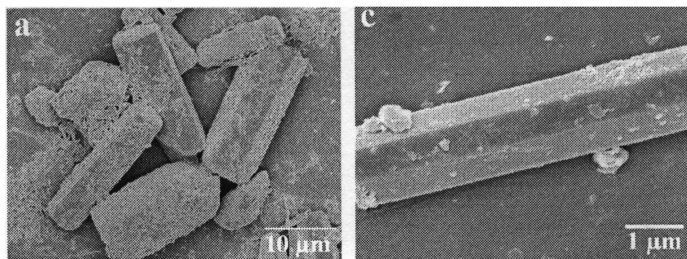


Fig. 3 FE-SEM images of as-prepared MoO_3 samples with different addition amount of HNO_3
(a) 5 mL; (b) 10 mL (Fig. 1c); (c) 15 mL

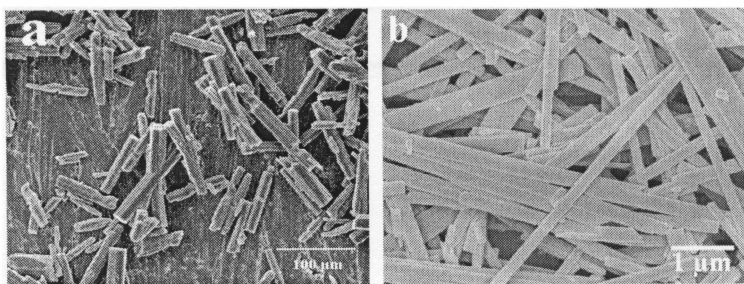


Fig. 4 FE-SEM images of as-prepared MoO_3 samples under the same experimental condition
but with different storage period of AHM precursor solutions
(a) Fresh AHM saturated solution; (b) aged AHM saturated solution

MoO_3 samples under the same experimental conditions but with the different storage period of the AHM precursor solutions. The fresh solution was used immediately after preparation, and the aged solution was kept at least 15 days at room temperature after preparation. Regular and well-proportioned MoO_3 hexagonal prism was obtained when the fresh solution was used (Fig. 4a). However, homogeneous MoO_3 nanobelts, which belonged to $\alpha\text{-MoO}_3$ according to the XRD analysis afterward, were synthesized when the aged solution was used. According to the experiment results, the storage time of the saturated AHM precursor solution was critical to determine the microstructure of the final MoO_3 product.

The XRD patterns of the as-prepared molybdenum trioxide nanobelts and hexagonal prism are illustrated in Fig. 5. All the diffraction peaks of Fig. 5b can be indexed as an orthorhombic-phase MoO_3 (JCPDS 05-0508, $a = 0.3962$ nm, $b = 1.385$ nm, $c = 0.3697$ nm). An observation of the strong reflection peaks (020), (040) and (060) (Fig. 5b) reveals an oriented anisotropic growth of the analogically $\alpha\text{-MoO}_3$ nanobelts. The diffraction peaks of Figure 5a can be

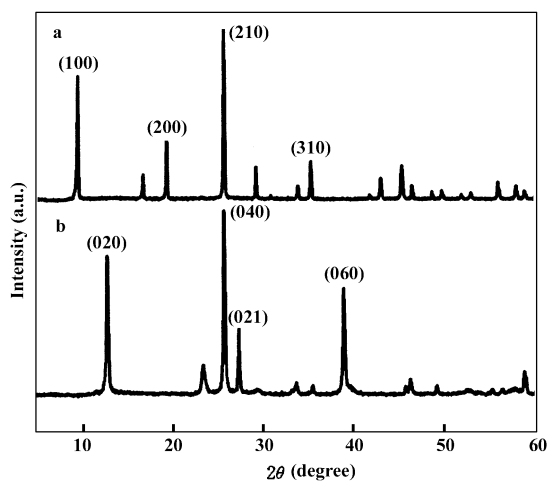


Fig. 5 XRD patterns for as prepared MoO_3 samples
(a) hexagonal prism; (b) nanobelts

indexed as a hexagonal-phase MoO_3 (JCPDS 21-0569), which is consist of the highly asymmetrical MoO_6 octahedra interconnected with their corners.

The FT-IR spectra of MoO_3 nanobelts and hexagonal prism were measured in the range of $4000 \sim 500$ cm^{-1} . The as-prepared nanobelts (Fig. 6b) showed three peaks at 550 , 866 , and 992 cm^{-1} , respectively. The peak at 992 cm^{-1} is attributed to the terminal $\text{Mo}=\text{O}$ stretching vibration, which is an indicator of the

layered orthorhombic MoO_3 phase. The band at 866 cm^{-1} is assigned to the Mo^{6+} stretching vibrations in

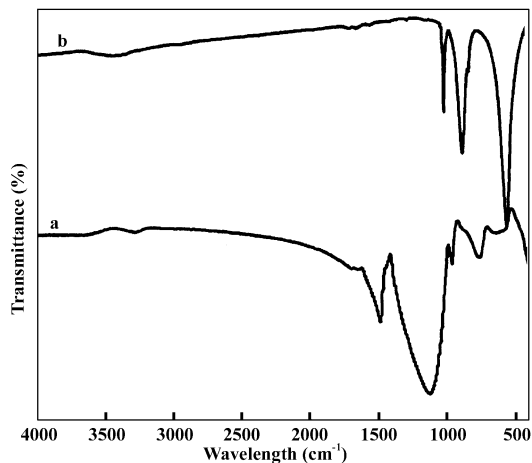


Fig. 6 FT-IR spectra for (a) MoO_3 hexagonal prism
(b) MoO_3 nanobelts

the Mo-O-Mo units. The signal at 550 cm^{-1} is associated with the bending mode vibration of the Mo-O-Mo entity, while the oxygen ion is shared by three Mo ions^[21, 22]. The broad band region in $3\ 436 \sim 1\ 643\text{ cm}^{-1}$ showed in Fig. 6 indicates that there is adsorbed water in the samples. It also can be seen that the peaks in Fig. 6a are different from the peaks in Fig. 6b. This might originate from the discrepancy in the structures and morphologies of the two samples.

2.5 The effect of the inorganic salts addition

Figure 7 demonstrates the inorganic salts influence on the MoO_3 morphology. According to the experiment results, it was found that the addition of FeCl_3 , $\text{Fe}(\text{NO}_3)_3$, and $\text{Ce}(\text{NO}_3)_3$ inhibited the formation of regular MoO_3 hexagonal prism. However, KBr was advantageous to the formation of molybdenum trioxide hexagonal prism. It is probable that the hexagonal-phase

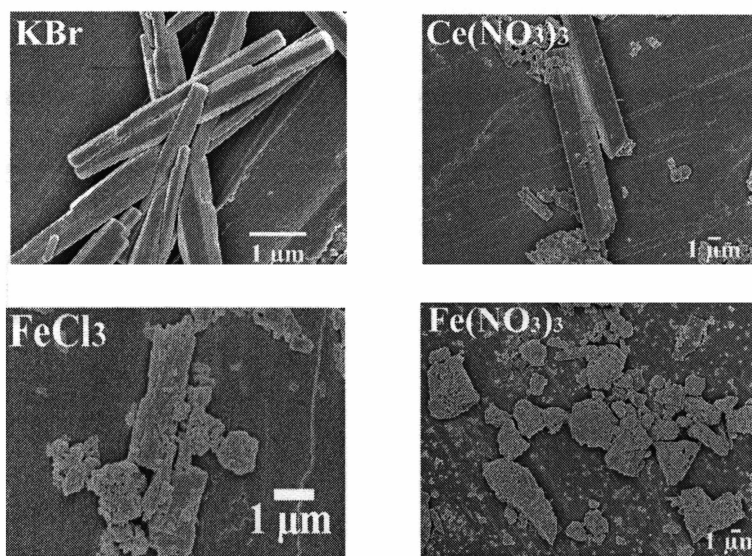


Fig. 7 FE-SEM images of as-prepared MoO_3 samples with adding the different varieties of inorganic salts but with the same concentration

MoO_3 is consisted of zigzag chains of MoO_6 octahedron which connected with corner, and the adjacent chains link up with cis-position to form sheet which accumulate and then extend in space to create one-dimensional hexagonal tunnel structure. This structure contains many defects in the tunnel, so the monovalent ion like Na^+ , K^+ , NH_4^+ etc^[23-25] can occupy the vacancies to stabilize the structure and compensate for the charge imbalance caused by Mo vacancies. Fe^{3+} and Ce^{3+} cannot embed the channel, so they have negative effect

to the structure stabilizing.

Figure 8 illustrates how the concentration of KBr affects the morphology of hexagonal MoO_3 . When the concentration of KBr was 0.5 mol L^{-1} the morphology of the MoO_3 product with 2.63% (determined by XRF) of K^+ was the best. The average diameter of the sample is between 200 nm and 800 nm, and their length range from $1\ \mu\text{m}$ to $8\ \mu\text{m}$. When the concentration was lower than 0.5 mol L^{-1} , there is a lack of K^+ to embed the tunnel to stabilize the hexagonal struc-

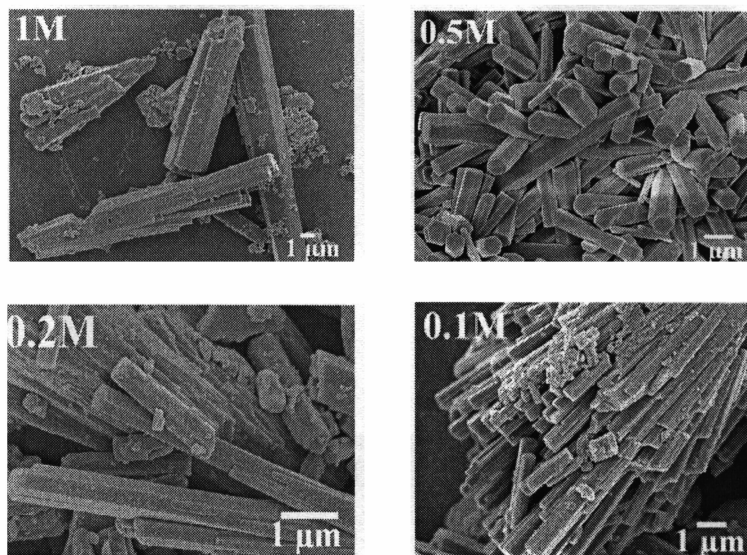


Fig. 8 FE-SEM images of as-prepared MoO_3 samples with adding the different concentrations of KBr solution

ture, so the obtained sample was defective. When the concentration was higher than 0.5 mol L^{-1} , the crystallization was promoted. The probable reason was the amount of K^+ which embedded the tunnel was increasing. And when the ongoing crystallization was unfinished, the other one was in the process. As a result, the product obtained was branched. In sum, an appropriate concentration of KBr is necessary to form uniform product.

3 Conclusion

In summary, we obtained the hexagonal-prism MoO_3 with the precursor solution of AHM and acidified by HNO_3 via a hydrothermal process. The best reaction temperature and time were $180 \text{ }^\circ\text{C}$ and 40 h, respectively. However, the hexagonal MoO_3 was transformed into sheet MoO_3 when the AHM precursor solution was kept for several days. Several inorganic salts were used in order to investigate their effect on the product morphology. It was found that the addition of KBr could effectively decrease the diameter of section while the regular hexagonal prism of MoO_3 was maintained.

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六棱柱状 MoO₃ 的水热合成、表征及其形貌控制研究

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摘要: 以钼酸铵为原料, 采用水热合成法制备出具有不同形貌的 MoO₃. 考察了反应温度、反应时间以及硝酸加入量对合成产物的影响. 同时比较了新鲜溶液和经过一定陈化时间后的溶液对产物形貌的影响. 实验结果表明: 用新鲜溶液在 180 °C 反应 40 h 后, 可以得到形貌较好的六棱柱状 MoO₃, 将反应溶液陈化一定的时间后再进行水热处理, 得到的产物形貌为片状. 同时还考察了无机盐的加入对 MoO₃ 形貌的影响. 结果表明, 加入 FeCl₃、Fe(NO₃)₃ 和 Ce(NO₃)₃ 抑制了 MoO₃ 六棱柱的形成, 加入 KBr 形成了规则的六棱柱状 MoO₃, 同时产物的截面直径也变小. 产物分别用场发射扫描电镜 (FE-SEM)、X-射线粉末衍射仪 (XRD) 和傅立叶变换红外光谱仪 (FT-IR) 进行了表征.

关键词: 水热合成法; MoO₃; 晶体形貌; 表征