Preparation of MoO_x (x = 2, 3) Crystallites Influenced by Hydrochloric Acid†

HANMEI HU*, JUNCHAN XU, XINQING GE, MEI SUN, HAN XUAN and KEHUA ZHANG

School of Materials and Chemical Engineering, Anhui Jianzhu University, Hefei, P.R. China

*Corresponding author: E-mail: hmhu@ustc.edu

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In this work, one-pot hydrothermal route has been presented to synthesize 3D MoO₂ nanoplate-based microspheres and 1D MoO₃ nanobelts and nanowires. The products are characterized by X-ray diffraction, field-emission scanning electron microscopy and UV-visible absorption spectrum. The experimental results reveal that the dosage of hydrochloric acid seriously influences the phase and morphology of molybdenum oxides. The optical properties of the synthesized 3D MoO₂ nanoplate-based microspheres and 1D MoO₃ nanobelts and nanowires are studied through the UV-visible absorption spectra.

Keywords: Molybdenum oxides, Hydrothermal synthesis, Optical property.

INTRODUCTION

Molybdenum oxides MoO_x (x = 2, 3), an important semiconductor and has been widely used in electrode materials, catalyst, gas sensing, photochromic devices¹⁻⁴ due to their multiple valence and high thermal and chemical stability. MoO₂ crystallizes mainly in three polymorphic forms⁵, including monoclinic, tetragonal and hexagonal phase. Wherein the monoclinic and tetragonal phases are common forms and the hexagonal phase is the unstable phase. MoO₃ also exists in three polymorphs⁶, *i.e.*, orthorhombic α -MoO₃, monoclinic β -MoO₃ and hexagonal *h*-MoO₃. Among them, α -MoO₃ is a thermodynamically stable phase, β -MoO₃ and hexagonal *h*-MoO₃ are attributed to metastable phases. Up to date, a great deal of efforts have been made to synthesize molybdenum oxides with different morphologies, including MoO₂ nanorods⁷, MoO₂ nanowire arrays⁸, MoO₂ hollow microchannels⁹, MoO₂ hollow core-shell microspheres¹⁰, MoO₃ nanorods¹¹, MoO₃ whiskers¹², MoO₃ nanobelts⁶, MoO₃ hollow microspheres¹³, MoO₃ flower-like nanobelt arrays¹⁴, *etc.* Herein, we demonstrate that 3D MoO₂ nanoplate-based microspheres and 1D MoO₃ nanobelts and nanowires are controllably synthesized through an easily operated hydrothermal method. It is worthwhile to note that MoO_x (x = 2, 3) products with special morphology can be successfully fabricated by only slightly tuning the dosage of hydrochloric acid in our designed reaction system.

EXPERIMENTAL

General procedure: In a typical procedure, 1 mmol (NH₄)₆Mo₇O₂₄·4H₂O (AHM), 2 mmol citric acid (C₆H₈O₇·H₂O) and 3 mmol Na₂CO₃ were successively dissolved into 25 mL (or 15mL) distilled water in a 40 mL Teflon-lined stainless steel autoclave. After stirring for 15 min, 5 mL (or 15 mL) diluted HCl (5 %) was subsequently added into the above solution. The solution total volume was kept at 30 mL. The obtained reaction mixture was stirred for an additional 0.5 h. Then, the autoclave was sealed and maintained at 200 °C for 12 h. After cooling down to room temperature naturally, MoO₂ (or MoO₃) precipitation was filtered out, washed with distilled water and ethanol for several times and then finally dried in a vacuum at 60 °C for 6 h. The related comparative experiments were listed in Table-1.

Detection method: The phases of samples were analyzed by X-ray diffraction (XRD) on a Philips X'Pert PRO SUPER X-ray diffractometer. The morphologies of the obtained products were recorded on a Field-emission scanning electron microscope (FESEM, JSM-6700F). The optical properties of the samples were investigated by using a UV-visible spectrophotometer (UV-5500PC).

RESULTS AND DISCUSSION

X-Ray diffraction technique was used to demonstrate the phase and crystal structure of as-prepared molybdenum oxides

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TABLE-1
 EXPERIMENTAL CONDITION OF SAMPLES AT 200 °C, TIME 12 h

No.	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O (mmol)	Citric acid (mmol)	Na ₂ CO ₃ (mmol)	5 % HCl (mL)	H ₂ O (mL)	Phase of products
1	1	2	3	5	25	Monoclinic MoO ₂
2	1	2	3	15	15	MoO ₃ (main phase: orthorhombic)
3	1	2	3	0	30	Hexagonal MoO ₂ and monoclinic MoO ₃
4	1	2	3	10	20	Orthorhombic MoO ₃ and monoclinic MoO ₂
5	1	2	3	25	5	Monoclinic MoO ₂ and orthorhombic MoO ₃

products, as shown in Fig. 1. Fig. 1(a) is the XRD pattern of the products prepared with the dosage of 5 mL HCl (5 %). All the diffraction peaks can be indexed as monoclinic MoO₂, in good agreement with the reported data (JCPDS No. 32-0671). Fig. 1(b) is the XRD pattern of the products obtained with the adding amount of 15 mL HCl (5 %). Most of the reflection peaks can be indexed to the orthorhombic phase of α -MoO₃ (JCPDS No. 35-0609). Three peaks with lower intensity (Marked by “#” in Fig. 1(b)) can be attributed to hexagonal h-MoO₃ (JCPDS No. 21-0569), which is one type of metastable phase of MoO₃.

Fig. 1. XRD patterns of (a) MoO₂ microspheres and (b) MoO₃ nanobelts and nanowires

Fig. 2(a) and (b) present the FESEM images of MoO₂ products (sample 1), which indicate that the products are composed of irregular sphere-like microcrystals with the sizes of 1.3-3.5 μ m. From the enlarged image of an individual microsphere [the inset of Fig. 2(a)], we can see the building blocks are nanoplates with the thicknesses of 60-90 nm. Fig. 2(c) and (d) show the morphology of MoO₃ products (sample 2), which indicate that belt-like (70 %) and wire-like (30 %) are found in the products. The widths and thicknesses of MoO₃ nanobelts are 100-200 and 30-50 nm, respectively and the

Fig. 2. (a,b) FESEM images of MoO₂ products, (c,d) FESEM images of MoO₃ products

lengths are in the range of 10-20 μ m. The diameters and the lengths of MoO₃ nanowires are estimated to be 30-40 and 15-25 μ m, respectively.

In the present designed synthetic system, the usage and amount of hydrochloric acid play important roles in controlling the phase and morphology of molybdenum oxides. To reveal the leverage of hydrochloric acid, a series of comparative experiments were carried out by only changing the dosage of hydrochloric acid while keeping other conditions unchanged. The experimental results were shown in Fig. 3. If HCl was not used, only little products (Sample 3) were obtained [Fig. 3(a) and (b)]. From the XRD pattern of Fig. 3(a), it may deduce that the main phase was unstable hexagonal phase of MoO₂ (JCPDS No. 50-0739), which was scarcely reported in the literature. In addition, a small quantity of monoclinic β -MoO₃ (JCPDS No. 80-0347) was also detected [marked by “*” in Fig. 3(a)], which was another type of metastable phase of MoO₃. The morphologies of products were submicrospheres with diameters of 500-1000 nm and some spheres tended to aggregate together to form multiple microspheres [Fig. 3(b)].

When 10 mL HCl was added into the reaction solution, the obtained products (sample 4) were the mixture in of major hexagonal MoO₃ and minor monoclinic MoO₂ (marked by “*” in Fig. 3(c)). According to the corresponding morphology displayed in Fig. 3(d), MoO₃ nanobelt-based bundles as well as some MoO₂ microspheres were observed and these nanobelts tended to aggregate together to form sheet-like microstructure. if the dosage of HCl was increased to 25 mL, the synthesized products (sample 5) were the mixture of major monoclinic MoO₂ and minor hexagonal MoO₃ (marked by “*” in Fig. 3(e)). From the correlative picture of Fig. 3(f), bigger

Fig. 3. XRD patterns and FESEM images of the products prepared at different conditions: (a,b) 0 mL 5 % HCl; (c,d) 10 mL 5 % HCl; (e,f) 25 mL 5 % HCl

MoO_2 microspheres and longer MoO_3 belt-based bundles were easily distinguished.

Based on the comparative experimental analysis, a conclusion could be drawn that the dosage of HCl really influenced the phase and morphology of MoO_x . At lower acidity (5 mL 5 % HCl), Mo(VI) were completely reduced to Mo(IV) by citric acid and pure monoclinic MoO_2 nanoplate-based microspheres could be obtained (sample 1). At moderate acidity (15 mL 5 % HCl), the reduction reaction were effectively restrained and MoO_3 nanobelts and nanowires were produced (sample 2). However, at higher acidity (25 mL 5 % HCl), Mo(VI) were partially reduced to Mo(IV) by excessive reducing acid HCl (sample 5). So, the desired molybdenum oxides products could be successfully achieved by adjusting the appropriate dosage of HCl in this system.

Fig. 4(a) and (b) exhibit the UV-visible absorption spectrum as well as band gap energy (inset) for MoO_2 microspheres and MoO_3 nanobelts and nanowires. The optical band gap E_g can be determined by the Tauc's equation of $(\alpha h\nu)^n = B(h\nu - E_g)$ for a semiconductor, where B is the edge-width parameter, $h\nu$ is the photon energy and the value of n is 2 for allowed direct transition of MoO_x . The plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in the inset of Fig. 4. By extrapolating the straight line to $(\alpha h\nu)^2 = 0$, the band gap E_g of MoO_2 microspheres is calculated to be 3.92 eV and that of MoO_3 nanobelts and nanowires is estimated to be 3.06 eV.

Conclusion

A simple and effective route is presented to controllably prepare nanoplate-based 3D MoO_2 microspheres and 1D MoO_3 nanobelts and nanowires. In the present designed reaction system,

Fig. 4. UV-visible absorption spectrum and band gap energy (inset) of (a) MoO_2 microspheres and (b) MoO_3 nanobelts and nanowires

the introduction and amount of hydrochloric acid is found play important roles in controlling the phase and morphology of molybdenum oxides. According to the UV-visible absorption spectrum, the band gap E_g of MoO_2 microspheres is calculated to be 3.92 eV and that of MoO_3 nanobelts and nanowires is estimated to be 3.06 eV.

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