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RESEARCH ARTICLE

**CHEN Jiu-ju, YANG Hai-bin, CHANG Lian-xia,
FU Wu-you, ZENG Yi, ZHU Hong-yang, ZOU Guang-tian**

Sonochemical preparation and characterization of photochromic MoO_3 nanoparticles

Abstract The effect of ultrasound irradiation on molybdenum trioxide has been investigated. Under ultrasonic irradiation, spherical-like MoO_3 nanoparticles were obtained, while bulk-like MoO_3 nanoparticles were prepared without ultrasonic irradiation. The changes in the physicochemical properties of MoO_3 have been investigated using techniques such as X-ray powder diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and ultraviolet and visible spectroscopy (UV-vis). The physicochemical changes of MoO_3 due to ultrasound irradiation have been attributed to the sonochemical cavity collapse onto the molybdenum trioxide particles. The ultrasonically prepared particles can also greatly improve the photochromism efficiency.

Keywords ultrasonic, MoO_3, photochromic

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1 Introduction

Ultrasound irradiation is widely used in the field of materials science. In recent years, the chemical effects of ultrasound have come under investigation with respect to the acceleration of chemical reactions and the synthesis of new materials. These effects arise from a process called acoustic cavitation [1]: the formation, growth and implosive collapse of the bubbles in a liquid, which produces unusual chemical and physical environments. Some extreme conditions, such as extremely high temperatures (> 5000 K), pressures (> 20 Mpa), and cooling rates (> 10^{10} $K \cdot s^{-1}$) can be obtained during acoustic cavitation. These may lead to many unique properties in the irradiated solution. Therefore ultrasound irradiation has been explored to prepare nanoscale metals, metal oxides, and nanocomposites [2–10].

Molybdenum trioxide is considered as being potentially important as a future display material [11, 12]. Bronzes based on molybdenum trioxide, for example, are being studied in reference to their application in high power batteries [13, 14]. Molybdenum oxides are also of fundamental significance to the catalytic community and supported molybdenum oxides have been used as industrial catalysts [15, 16].

Experimentally, however, it has been observed that the collapsing bubble size is about 40 μm [17]. The damage associated with jet formation cannot occur if the solid particles are smaller than the collapsing bubble size. In these cases, the shock waves created by the homogeneous cavitation, however, can create high velocity interparticle collisions. The cavitation and shockwaves in slurry can accelerate solid particles to high velocities and the resultant collisions are capable of inducing dramatic changes in surface morphology, composition, and reactivity. Agglomeration of metal powders, fragmentation of brittle solids, enhancement of the reactivity of metals, enhancement of rates of intercalation in layered materials, and enhancement of the rates of catalytic reactions [18] are some of the observed mechanochemical effects of ultrasound.

In the present study, the effect of ultrasound irradiation on MoO_3 has been investigated. The purpose of our investigation was to find out which physicochemical properties (structure, morphology, composition, etc.) are changed during the process of ultrasound irradiation so as to show that ultrasonic irradiation may be a very effective method for preparing MoO_3 nanospheres.

CHEN Jiu-ju, YANG Hai-bin (✉), CHANG Lian-xia, FU Wu-you, ZENG Yi, ZHU Hong-yang, ZOU Guang-tian
National laboratory of Superhard Materials, Jilin University, Changchun 130012, China
E-mail: hai-bin-yang@hotmail.com

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2 Experimental

2.1 Preparation of MoO_3 nanoparticles

All chemicals were of analytical grade and used without further purification. Ammonium heptamolybdate tetrahydrate [AHM: $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] was dissolved in distilled water and was made up with concentration of 0.02 M at room temperature. In a typical preparation procedure, with the presence of ultrasonic (40 kHz) and mechanical agitation, pure glacial acetic acid was carefully added into a 100 mL AHM solution, and then, 100 mL absolute ethyl alcohol was slowly dropped in via a dropping funnel. Amount of white precipitation was obtained when the acidified AHM precursor solution was stored for 2 h. The produced intermediate precipitation was dried at room temperature for 24 h and then was sintered at 350 ˚C for 2 h in a muffle furnace to produce MoO_3 nanoparticles.

2.2 Characterization

The phase structure of nanoparticles synthesized from AHM was identified by X-ray powder diffraction (XRD) using Cu kα radiation (λ = 1.541 78 Å). Data were collected in steps of 0.05˚ with a count time of 1 s, at an operating potential of 40 kV and a current of 100 mA. The morphology, size and absorption of these products were determined by field emission scanning electron microscopy (FE-SEM, JSM-6700F) and UV-vis spectra.

3 Results and discussions

Figure 1 (a) shows the XRD pattern of the sample synthesized under ultrasonic condition, which reveals that these products are high-purity MoO_3 nanoparticles. All the reflections can be indexed to the pure orthorhombic MoO_3 with lattice parameters a = 3.962 Å, b = 13.88 Å, c = 3.700 Å, which agree well with the reported values (JCPDS card No. 76-1003, a = 3.962 Å, b = 13.85 Å, c = 3.696 Å).

Shape and size of the synthesized particles were observed by FE-SEM images. Figure 2 (a) shows that under ultrasonic condition, the obtained nanoparticles are almost spherical in shape with a narrow size distribution; the average size is about 70 nm. However, Fig. 2 (b) shows that the particles obtained without ultrasound radiation are bulk-like. The obvious difference in shape between Fig. 2 (a) and Fig. 2 (b) may be due to the following reasons.

The effects of ultrasound on chemical systems have been strongly associated with the phenomena known as cavitation. There are many types of cavitation which may form within a liquid under the influence of favorable physical conditions. However, a large proportion of the chemical and physical effects are strongly associated with inertial (transient) cavitation. This phenomenon is characterized by the expansion and subsequent rapid collapse of voids or bubbles within a liquid as the result of suitable physical conditions. The generation of inertial cavitation is often achieved through the application of an ultrasonic sound field within a liquid, although some instances of sonochemical effects induced by inertial cavitation can be found employing flows.

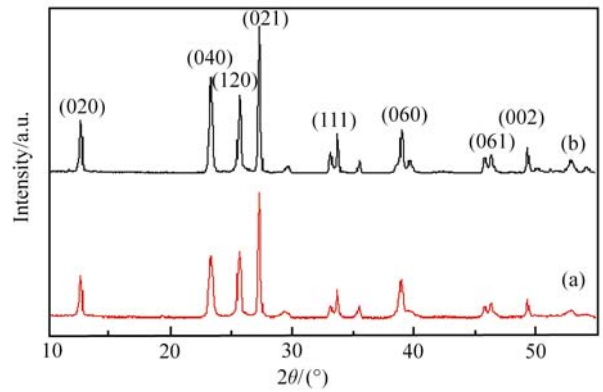

Fig. 1 XRD patterns of as-synthesized MoO_3: **(a)** with ultrasound irradiation and **(b)** without ultrasound irradiation.

During the ultrasonic treatment, the dissolved material is subjected to microcavitation formed in rarefaction cycle when the bubbles undergo unsymmetrical collapse near the solid, which causes an inward rush of liquid known also as microstreaming. Thus, certain energy is provided to sufficiently overcome most of the weak bonds such as the hydrogen bonding and the van der Waal forces that exist in aggregated particles, but is much lower than the chemical bonding energy.

It has been known that MoO_3 nanoparticles can show a strong photochromic effect [19]. Because of this, we put the MoO_3 solution under the sunlight for different time (0 h, 2 h, 4 h, 6 h) and the results are shown in Fig. 3. It is obvious that the colour of the ultrasonically prepared solution is changed more and more obviously with the increasing time. Meanwhile, having compared Fig. 3 (a) with Fig. 3 (b), it is found that the color changes faster for a solution with ultrasound irradiation than a solution without ultrasound irradiation. To further test the effect of absorption, some UV-vis absorption has been measured, which can be seen in Fig. 4.

The dependence of the UV-vis absorption spectra of the MoO_3 sample (prepared under ultrasonic condition) on the irradiation time of sunlight is shown in Fig. 4 (a). The change in absorbance is seen across the visible range; the largest change occurs from 550 nm to 800 nm. For example, the change of absorbance at 750 nm is 3.43 after the irradiation of the nanoparticles for 6 h. For comparison, a series of UV-vis spectra of bulk-like MoO_3 was also measured at different irradiation time under the same condition and the results are shown in Fig. 4 (b). The change of absorbance at 750 nm is only 0.47 for the bulk-like MoO_3 after irradiation with sunlight for 6h. Thus, the color change in the nanopar-

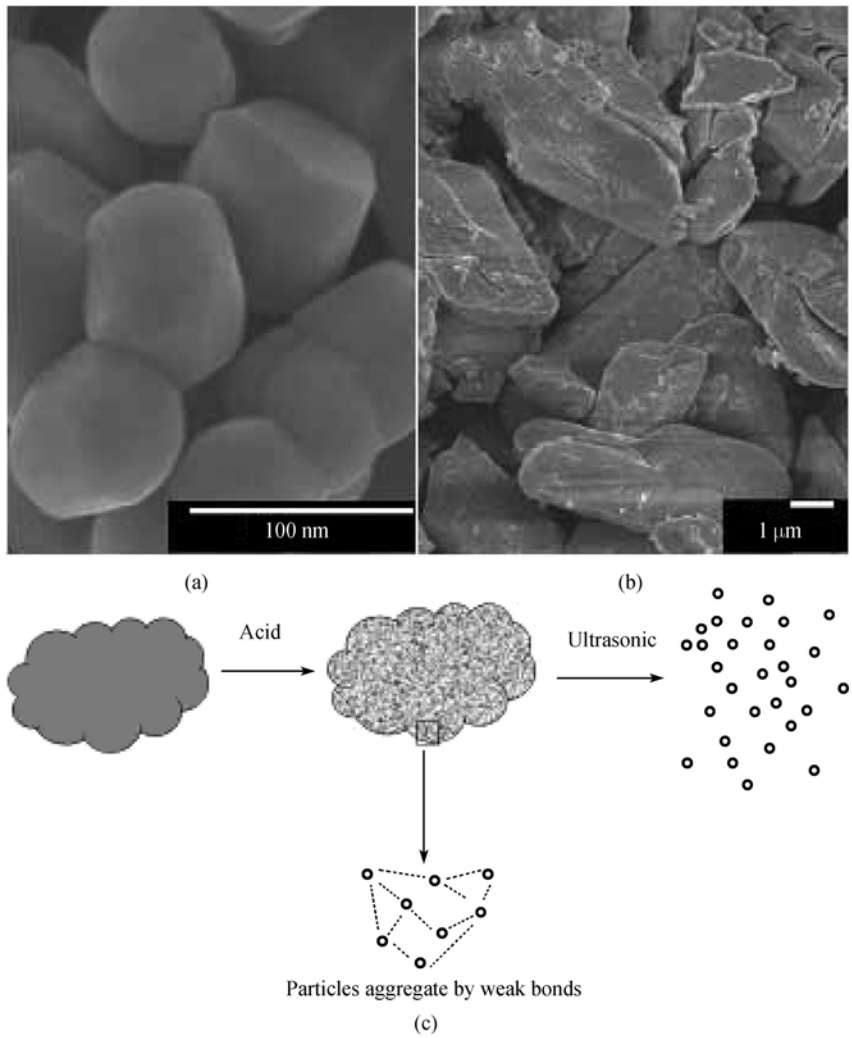

Fig. 2 FE-SEM images of as-synthesized MoO_3: **(a)** with ultrasound irradiation; **(b)** without ultrasound irradiation; **(c)** schematic model proposed for the effect of ultrasonic treatment under present synthesis. The dotted lines indicate the weak bonds.

ticles is 7.3 times stronger than that of the bulk-like sample under similar irradiation conditions.

Fig. 3 MoO_3 solution on the distinct irradiation time of sunlight **(a)** with ultrasound irradiation and **(b)** without ultrasound irradiation, respectively.

Several models have been proposed to explain the coloration mechanism: Deb suggested that coloration was due to the formation of F centers [20]; Schirmer and Salje postulated that dipolaron injection caused the color change [21]; Faughnan *et al.* proposed that coloration was due to simultaneous injection of cations and electrons [22]. The Faughnan model can effectively explain our experimental result by the following equation:

$$MoO_3 + xe^- + xH^+ \rightarrow H_xMoO_3$$

In the case of MoO_3, the injected electrons were trapped by some Mo^{6+}, forming Mo^{5+}, and coloration is attributed to the intervalence charge-transfer transition between Mo^{6+} and the newly formed Mo^{5+}. The intercalated H_xMoO_3 is known as the molybdenum bronze.

In addition, due to the ultrasound effect, the MoO_3 particles in the solution can be distributed symmetrically so that the specific surface area of nanoparticles is larger, which can reduce response time and improve the coloration efficiencies of the solution.

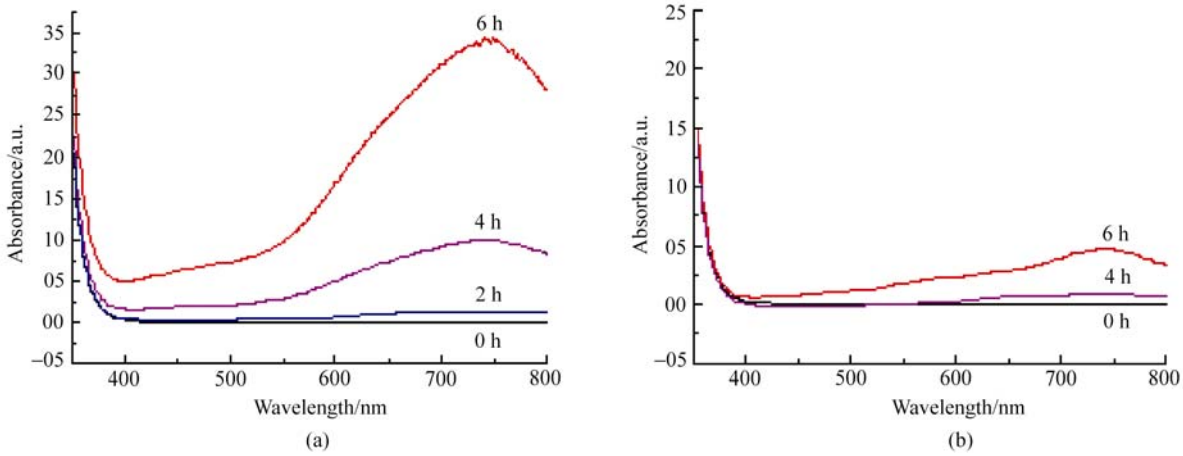

Fig. 4 UV-vis spectra of **(a)** spherical-like MoO_3 nanoparticles and **(b)** bulk-like MoO_3 as a function of the irradiation time.

4 Conclusions

In this paper, spherical-like MoO_3 nanoparticles have been successfully obtained under ultrasonic irradiation, which proves that ultrasonic irradiation is a very effective method for preparing MoO_3 nanospheres. The changes in the physicochemical properties of the MoO_3 were followed by a variety of techniques including XRD, FE-SEM and UV-vis. On irradiation with ultrasound, MoO_3 particles change their morphology and a reduction in particle size. These observed changes have been explained on the basis of interparticle collisions driven by ultrasound irradiation.The obtained MoO_3 nanoparticles under ultrasonic condition were also found to show improved photochromism effect.

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