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The dual-wavelength excitation photochromic behavior of organic induced MoO_3 powders synthesized via a hydrothermal route

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ABSTRACT

Production of molybdenum oxide materials with dual-wavelength excitation photochromism which could be motivated by UV and visual light is attractive. Here, we have successfully synthesized the novel dual-wavelength excitation photochromic molybdenum oxide (MoO_3) powders with organic inducers. The variety and amount of organic inducers have great impact on the final product morphologies. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), BET nitrogen physisorption apparatus, ultraviolet–visible diffuse reflectance spectroscopy (UV–vis), and color difference meter. The XRD spectrums of samples demonstrate that the as-obtained products are pure hexagonal phase. The non-induced MoO_3 powders present to be neat hexagonal prisms while the induced MoO_3 powders possess flower-like and yuba-like structures. In addition, we found that sample S3 got the optimized photochromic property. This could be attributed to the enhanced light harvesting from multiple light reflections and scattering in-between the cavities on the surface of spheroidal-flower structure.

1. Introduction

Photochromism of transition metal oxides has received considerable attention because of potential applications in information display devices [1,2]. These oxides can be deeply colored with optical irradiation of the appropriate energy (photochromism). Molybdenum oxide (MoO_3) has been the most extensively investigated materials of all the transition metal oxides [3–9]. Fibrous MoO_3 have been synthesized via a novel, one-step solvothermal procedure [10]. One-dimensional nanostructures of orthorhombic molybdenum trioxide have been synthesized in the forms of ribbons or rods via acidification under hydrothermal conditions at 140–200 °C [11]. Novel metastable hexagonal phase MoO_3 nanobelts were prepared by a simple hydrothermal route from peroxomolybdate solution with the presence of sodium nitrate as a mineralizer [12].

Multi-wavelength materials with constant wave-length spacing have attracted extensive interest for many years, because of their wide potential applications in spectroscopy and optical communication [13]. A multi-wavelength excited material is able to be motivated by multiple wavelength ranges of excitation light. As the materials are sensitive to multiple wavelength ranges of excitation light, especially in different light partition area, the photoexcitation process occurred under multiple excitation lights of different wavelength ranges. Using the multi-wavelength excitation theory in photochromic materials may efficiently promote the applications in smart windows and display devices etc., eventually making smart windows smarter and display devices more sensitive to light intensity in the surroundings.

The applications of transition-metal oxides as photochromic materials, however, are handicapped because most of these oxides require single UV-light excitation [14]. Recently, a breakthrough was reported in which MoO_3 materials, after induced by some special organic inducers (such as formaldehyde, n-propanol), exhibiting both UV-light and visible-light photochromism (i.e. dual-wavelength excitation photochromism) [15,16]. In view of this result, these investigations were carried out to probe into the enhancement mechanism as well as study the dual-wavelength excitation photochromism of MoO_3 powders through changing the content and species of organic inducers. Adding organic additives has been shown to enhance photochromic properties of MoO_3 [16–19].

2. Experimental

2.1. Preparation of the molybdenum oxide powders

All chemicals were of analytical grade purity and used as received without purification. The pure water was obtained from a Milli-Q synthesis system. In a typical procedure, the sodium molybdenum powder was dissolved by distilled water to a concentration of 0.1 M, and the $Na_2MoO_4 \cdot 2H_2O$ solution was acidified to a fixed pH of 1.0 by concentrated HCl solution (37–38 wt.%). After being stirred for 240 min, appropriate amounts of organic additives were added into

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the system. The amounts of alcohol were 0, 10, and 20 ml labeled S1, S2 and S3 respectively. The amounts of isopropanol and 1,2-propanediol were both 10 ml and labeled S4 and S5. These as-prepared precursors were transferred into the 100 ml Teflon-lined stainless steel autoclave. Then the autoclave was sealed and maintained at 120 °C for 48 h. After cooling down to room temperature, the product was collected and washed sequentially with water and ethanol, then finally dried at 60 °C in the vacuum.

2.2. Characterization

The crystal structure information of the resulting products were analyzed by X-ray diffraction (XRD, D8-FOCUS, Bruker AXS) with a Cu-K$_\alpha$ radiation source ($\lambda = 0.1541$ nm) and settings of 40 mA and 40 kV at a scanning rate of 0.01° per 0.05 s in the 2θ range from 5° to 75°. The surface morphologies were characterized by scanning electron microscopy (SEM, JSM-5610LV, Japan, 20 KV) and transmission electron microscopy (TEM, 100SX Rigaku, Japan). The texture properties of MoO_3 powders were determined by multi-point BET nitrogen adsorption (ASAP2020, Micromeritics). Furthermore, photochromic properties of the resulting products were tested by ultraviolet–visible diffuse reflectance spectroscopy (UV–vis, Shimadzu UV-2550, Japan) with $BaSO_4$ as the baseline correction, combined with color difference meter [20].

3. Results and discussion

3.1. Phase analysis

Fig. 1 shows the X-ray diffraction patterns of products prepared at 120 °C with different conditions. The XRD patterns clearly show that all the diffraction peaks of the products can be indexed to the hexagonal structure of MoO_3 (PDF Card no. 47-0812) with a space group P 6_3/m (176). No other impurities were detected in the final products. The results indicate that the addition of organic reagent has no obvious effects on the crystalline phase of MoO_3 products. However, the relative intensity of peaks of induced powders is higher than the non-induced powders, which reveals that the induced powders crystallize better than the non-induced powders.

3.2. Microstructure investigations

The morphologies of the samples are demonstrated in Figs. 2 and 3. The organic inducers have great effect on the morphology and particle size of MoO_3 powder. The morphology of the non-induced MoO_3 powder is shown in Fig. 2(a–b), which indicates that the obtained product consists of randomly accumulated hexagonal prisms, with an average diameter of 4 μm, a length of about 40 μm, and an aspect ratio of merely 10. It can be observed from Fig. 2(c–f) that the alcohol-induced MoO_3 powder presents a flower-like morphology which is composed loosely packed nanofibers with uniform length, similar shape and clear particle boundaries; each MoO_3 nanofiber has a diameter of about 50 nm, a length of about 2.5 μm and an aspect ratio of about 50. Besides, the two alcohol-induced MoO_3 powders differ significantly in the shape: S2 presents to be chrysanthemum with plentiful filamentous petals, and S3 presents a mesoporous spherical morphology which seems to be spheroidal-flower. Specifically, there are lots of sunken areas on the surface of the spheroidal-flower. So the alcohol-induced MoO_3 powder exhibits much larger specific surface area compared with the non-induced MoO_3 powder, mainly attributed to the multi-pore structure and smaller particle size. When isopropanol was added, the MoO_3 powder is composed of flower-like structures as well. It is mentioned that these flower-like structures of isopropanol-induced MoO_3 powder are apparently inferior to that of alcohol-induced powders due to the non-uniform shape and unclear boundary. In addition, sample S5 is composed of irregular yuba-like nanoparticles, most of which messily aggregate together, with massive irregular blocks surrounded (shown in Fig. 3(i–j)).

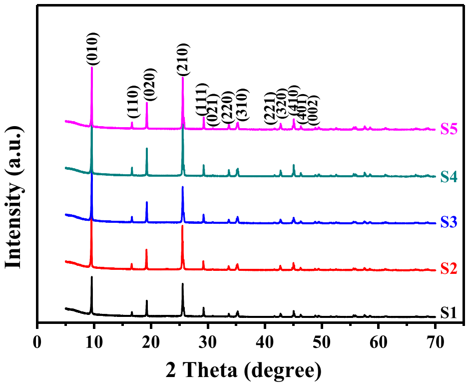

Fig. 1. XRD patterns of MoO_3 synthesized with different conditions: S1: without any additives, S2: with 10 ml alcohol, S3: with 20 ml alcohol, S4: with 10 ml isopropanol and S5: with 10 ml 1,2-propanediol.

The microstructures of the as-prepared MoO_3 products with different conditions were further investigated by TEM, and the results were shown in Fig. 4. Shown in Fig. 4a is a TEM image taken from the sample without any additives. It clearly shows the presence of hexagonal prism, in accordance with SEM results in Fig. 2(a–b). It is observed that both alcohol-induced and isopropanol-induced samples are composed of nanofibers (shown in Fig. 4c, e, g). However, the microstructures of isopropanol-induced product possess larger diameter than the alcohol-induced. These results are in good agreement with those obtained from the SEM images, suggesting that the well-dispersed and flower-like arranged nanofibers are in the right of the nanofibers in the TEM images. Fig. 4d displays that the propanediol-induced product are composed of irregular yuba-like nanoparticles, which is in accordance with SEM images in Fig. 3(i–j). According to the results of SAED patterns (shown in Fig. 4b, d, f, h, j), the samples are hexagonal and well-crystallized, consistent with the XRD analysis.

Based on the obtained results, the possible formation process of the MoO_3 with various morphologies can be proposed according to the schematic illustration of mechanism shown in Fig. 5. Fig. 5(a) summarizes the major stages involved in the formation of the MoO_3 powders without any additives. Firstly, the MoO_3 precursors formed via the reaction of sodium molybdate and hydrochloric acid solution. Then MoO_3 nucleation and subsequent growth occurred when the supersaturation of the solution approached a certain value, with the increase of the temperature and pressure in the hydrothermal system [21]. As the products belong to *h*-MoO_3, the primary particles may ultimately grow into the neat hexagonal prismatic structure resulting from the inherent symmetry in hexagonal system [22].

Fig. 5(b–d) shows the hydrothermal formation process of the flower-like MoO_3. It is therefore believed that the flower-like structures undergo three main steps in the following order: 1) nucleation/growth of the primary MoO_3 nanofibers, 2) the primary MoO_3 nanoflakes oriented aggregating to from the secondary nanoflakes and 3) self-assembly of the secondary flakes and a further growth giving rise to the formation of the product with the 3D morphologies. The organic additives play remarkable roles in all growth stages, which act not only as the structure-oriented agent but also as a soft-template [23]. When the alcohol inducers add, the hydroxy (–OH) groups of alcohol molecules are easy to form hydrogen bonds with the oxygen atoms in MoO_3 crystal. Because the distribution of the oxygen atoms in MoO_3 crystal is much close between the zigzag chains paralleling to the b-axis, and followed by that of the vertical direction of the c-axis, the directed adsorption layers of alcohol molecules are formed on the surface of MoO_3 crystal, which promotes the MoO_3 crystal growth along the b-axis direction, and hinders the crystal from growing in the c-axis direction further, resulting in the formation of nanofibers with a large