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Surfactant-free hydrothermal synthesis, growth mechanism and photocatalytic properties of $PbMoO_4$ polyhedron microcrystals

Lei Zhang, Dianrang Bai, Min Zhou, Chengling Pan *

Laboratory of Multiscale Materials and Molecular Catalysis, School of Materials Science and Engineering, Anhui University of Science and Technology, Huainan, Anhui 232001, People's Republic of China

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Abstract In the present paper, $PbMoO_4$ polyhedron microcrystals were prepared via a facile hydrothermal synthetic route in the absence of any surfactant, employing $Pb(NO_3)_2$ and $Na_2MoO_4 \cdot 2H_2O$ as starting materials. The phase and morphology of the product were characterized by powder X-ray diffraction (XRD), energy dispersive spectrometry (EDS), Raman spectrum, FT-IR spectroscopy and scanning electron microscopy (SEM). Some factors influencing the morphology of the final product have been investigated. Experimental results indicated that appropriate volume of glycerol could effectively regulate the nucleation rate and contribute to the formation of $PbMoO_4$ microcrystals of large size. A possible growth mechanism of the $PbMoO_4$ polyhedron was proposed based on the experimental results. Moreover, the photocatalytic properties of the products were studied.

1. Introduction

Metal molybdate materials with scheelite-type tetragonal structure exhibit interesting optical, electronic and magnetic properties and thus have great potential applications in fields such as photoluminescent materials, microwave devices, optical fibers, scintillator materials, humidity sensors, and catalysis [6,31,26,27]). As one of the members, $PbMoO_4$ has attracted considerable attention and has been widely used in optical-instrument engineering, photoconductivity and as a UV-light-driven photocatalyst [14,8,9]. Traditionally, $PbMoO_4$ is prepared via high temperature solid-state reactions. In recent years, several solution-phase routes have been employed to controllably prepare this family of materials [5,1,2,12,13,10]. For example, Shen et al. have designed a facile CTAB-assisted hydrothermal process to prepare $PbMoO_4$ microcrystals with preferentially exposed (0 0 1) facets [15]. Xing et al. reported the successful preparation of well-defined and uniform $PbMoO_4$ polyhedral crystals via a microemulsion-based solvothermal method [21]. Usually, organic surfactants are introduced to the reaction medium and served as templates or structure directing agents in these synthetic processes, which can effectively modulate the growth of the structure and morphology of the products. In most cases, the pure product

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* Corresponding author. Tel./fax: +86 554 6668649.
E-mail address: clpan@aust.edu.cn (C. Pan).

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is obtained only after the complete removal of the surfactants. Therefore, it makes the experimental process more complicated. In addition, most of the organic surfactants are high in cost. However, up to now, reports on the preparation of $PbMoO_4$ polyhedron microcrystals in the absence of any surfactant remain uncommon.

Herein, we report a facile surfactant-free solution-phase synthetic approach for the preparation of the $PbMoO_4$ polyhedron. By controlling the experimental parameters, such as reaction time, temperature and the volume ratio of water and glycerol, the $PbMoO_4$ polyhedron has been successfully fabricated. A possible growth mechanism of the product is proposed. In addition, the photocatalytic properties of the products were studied.

2. Materials and methods

All reagents were purchased from the Shanghai Chemical Company and used without further purification. In a typical preparation procedure, $Pb(NO_3)_2$ (0.001 mol) was dissolved in 5 mL of deionized water and 20 mL of glycerol. Then, 5 mL of deionized water containing 0.001 mol of $Na_2MoO_4 \cdot 2H_2O$ was slowly dropped into the above solution. The as-obtained solution was stirred for 10 min and transferred into a stainless-steel autoclave with a Teflon liner of 40 mL capability. After treating the mixture at 180 °C for 24 h, it was cooled to room temperature naturally. The product was collected, washed with deionized water and absolute ethanol, and dried in a vacuum at 60 °C for 6 h with a yield of 90%.

The products were characterized by X-ray powder diffraction (XRD) with a Shimadzu XRD-6000 powder X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å), recorded with 2θ ranging from 10° to 80°. SEM images of the products were obtained on field emission scanning electron microanalyser (Hitachi S-4800), employing the accelerating voltage of 10 kV. Energy dispersive X-ray spectroscopy, being attached to the scanning electron microscope, was used to analyze the composition of the sample. Raman spectrum was taken at room temperature in the spectral range of 100–1000 cm^{-1} using a JY HR800 Raman spectromicroscope. FT-IR spectrum was recorded for KBr-diluted samples using a Nicolet Magna 750 IR spectrometer at wavenumbers 400–4000 cm^{-1}. The UV–vis diffusion reflectance spectrum (DRS) of the sample was analyzed with a UV–vis spectrophotometer (UV-3600, Shimadzu, Japan). The Brunauer–Emmett–Teller (BET) surface area was measured using a Micrometrics ASAP 2010. Photoluminescence spectrum was recorded employing an Edinburgh FLSP 920 fluorescence spectrophotometer at room temperature.

Photocatalytic degradation of RhB, MO or phenol aqueous solution was conducted in an XPA-photochemical reactor (Xujiang Electromech-anical Plant, Nanjing, China) equipped with a 500 W high-pressure mercury lamp. An electric fan and cycled condensate water were used to prevent thermal catalytic effects. 0.01 g of photocatalyst was introduced into each of a series of Pyrex reactors containing 30 mL of dye solution (10 mg/L) or phenol aqueous solution (20 mg/L) at room temperature under air, respectively. Before the light was turned on, the solution was continuously stirred for 60 min in the dark to ensure the establishment of an adsorption–desorption equilibrium. During irradiation, ~3 mL of the suspension was continually taken from the reactor at given time intervals. The photocatalyst powder and the polluted solution were separated by a centrifugal machine. The MO, RhB and phenol concentration were analyzed through a UV–vis spectrophotometer (UV-3600, Shimadzu, Japan). Total-organic-carbon (TOC) concentrations in the solutions were checked on a TOC analyzer (TOC-V CPH, Shimadzu, Japan).

3. Results and discussions

The composition and phase of the as-obtained sample were examined by XRD and EDS. Fig. 1a depicts the XRD pattern of the product prepared at 180 °C for 24 h. All the reflection peaks can be indexed to a pure tetragonal phase $PbMoO_4$ with calculated lattice constants of a = 5.42 Å and c = 12.10 Å, which are in good agreement with the literature values (JCPDS file Card No. 74-1075). The strong and sharp diffraction peaks imply good crystallinity of the product. No other impurity peak is detected. Additional evidence of the formation of $PbMoO_4$ came from energy dispersion X-ray analysis. Fig. 1b shows the EDS spectrum of the as-prepared product. The peaks of Pb, Mo and O can be easily found. The C peak in the spectrum can be attributed to CO_2 adsorbed by the sample. Quantitative analysis of the sample gives Pb, Mo and O molar ratio of 1.0:1.1:3.6, which is close to the $PbMoO_4$ stoichiometry. The microstructure and morphology of the product were investigated by SEM. As shown in Fig. 1c, the as-prepared product is composed of abundant $PbMoO_4$ polyhedron microcrystals with relatively good dispersion. A high magnification SEM image shown in Fig. 1d reveals that the surface of such polyhedron microcrystals is very smooth and no nanoparticles of small size are attached.

Fig. 2a shows the Raman spectra of the $PbMoO_4$ sample. The Raman peak at 873.5 cm^{-1} can be assigned to the symmetric stretching vibration mode $v_1(A_g)$ of the $[MoO_4]$ clusters in the $PbMoO_4$ crystal. The peaks at 766.7 and 748.0 cm^{-1} correspond to the anti-symmetric stretching $v_3(B_g)$ and $v_3(E_g)$ vibration modes, respectively. Two modes at 300–400 cm^{-1} are interpreted as the stronger $v_2(A_g)$ and weaker $v_4(B_g)$ of the regular $(MO_4)^{2-}$ tetrahedrons. The A_g mode at 169.9 cm^{-1} for $PbMoO_4$ is much weaker than other modes. These results are consistent with other previous reports about $PbMoO_4$ [12,21]. Fig. 2b illustrates the transmittance FTIR spectrum of $PbMoO_4$ polyhedron microcrystals at 180 °C for 24 h. Only the strong transmittance mode is observed at 720–900 cm^{-1}, which can be specified as the Mo–O anti-symmetric stretching vibration of the $[MoO_4]^{2-}$ tetrahedrons [8].

As a general nonaqueous solvent with a relatively high boiling point, glycerol has been widely used in the so-called polyol synthesis of various metal and metal chalcogenide nanoparticles [11,18,24]. In this work, when the volume of glycerol was controlled at 0, 5 and 10 mL, nanoparticles were obtained (Fig. 3a–c). On increasing the volume of glycerol to 15 mL, the bulk of the product was comprised of $PbMoO_4$ polyhedrons (Fig. 3d). In addition, some nanoparticles of small sizes were attached to the surface of these polyhedrons. If the volume of glycerol was controlled at 20 mL, $PbMoO_4$ polyhedrons with a smooth surface appeared (Fig. 1). These results indicate that appropriate volume of glycerol plays an important role in the formation of such $PbMoO_4$ polyhedrons. As is well known, a crystal growth process includes nucleation and growth. If the

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