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Short communication

Photoluminescence and photocatalytic properties of uniform $PbMoO_4$ polyhedral crystals synthesized by microemulsion-based solvothermal method

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Abstract

Well-defined and uniform $PbMoO_4$ polyhedral crystals were successfully synthesized via a microemulsion-based solvothermal method. The structure and morphology of these crystals were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), micro-Raman (MR) spectroscopy and photoluminescence (PL) measurements. XRD and MR spectra confirmed that the $PbMoO_4$ polyhedrons have a scheelite-type tetragonal structure. FESEM micrographs show that uniform $PbMoO_4$ polyhedral crystals in the shape of regular 18-facet polyhedron with well-defined face contour can be prepared by microemulsion-based solvothermal method. The addition of nitrilotriacetic acid into the microemulsion reaction system was verified to play an important role in the formation of the uniform $PbMoO_4$ polyhedrons. An intense blue PL emission at room temperature was observed in these $PbMoO_4$ polyhedrons when they were excited with a 300 nm wavelength. The results of photocatalytic degradation of rhodamine B showed that these $PbMoO_4$ polyhedrons display excellent photocatalytic activity under ultraviolet-visible light irradiation.

Keywords: Nanostructure; Oxide; Sol–gel chemistry; Crystal structure; Luminescence

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1. Introduction

Metal molybdate materials with scheelite-type tetragonal structure have wide potential and practical applications in many fields, such as photoluminescence (PL), solid-state optical maser, optical fibers, scintillator materials, humidity sensor, magnetic materials and catalysts [1–5]. Lead molybdate ($PbMoO_4$), belonging to this so-called scheelite structure, have recently gained increasing attracting interest because of its applications, such as: acousto-optical deflectors, modulators, ion conductors and low-temperature scintillators in nuclear instruments [6–10].

In the past decades, $PbMoO_4$ has been prepared mainly by Czochralski crystal growth [7,11,12] and solid state reaction method [13]. Nevertheless, these approaches to the preparation of $PbMoO_4$ powders usually require complex experimental procedures, sophisticated equipment, and harsh synthesis conditions. In addition, in recent years, the controlled synthesis of molybdates crystallites with desirable shape accuracy, size, and crystal structure is of considerable interest because of its wide technological applications [14–18]. Therefore, wet chemical solution methods, such as hydrothermal [19,20], solvothermal [21], and microwave irradiation method [22] have been developed with the intention of minimizing these drawbacks. However, in some of these methods, there still are verified serious problems, mainly including polydisperse particle size distribution, and uncontrolled morphology. Therefore, it still remains a significant challenge to controllably synthesize $PbMoO_4$ crystals with homogenous and well-defined morphologies via facile routes.

In this paper, we report the controllable synthesis of $PbMoO_4$ monodispersed crystals with well-defined polyhedral shape via a facile microemulsion-based solvothermal method. Nitrilotriacetic acid (NTA) was selected as complexing agent

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with Pb^{2+} ions and added to the mircoemulsion system, which was proved to play an important role in the formation of uniform $PbMoO_4$ polyhedral crystals. The as-prepared $PbMoO_4$ polyhedral crystals are displayed to possess excellent photocatalytic activity in the photodegradation of rhodamine B (RhB) under ultraviolet-visible light irradiation.

2. Experimental details

2.1. Sample preparation

Lead acetate trihydrate ($Pb(Ac)_2 \cdot 3H_2O$, 99.5% purity, Sinopharm), nitrilotriacetic acid ($C_6H_9NO_6$, NTA, 98.5% purity, Sinopharm), sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$, 99.0% purity, Fuchen), hexadecyl trimethyl ammonium bromide (CTAB, 99.0% purity, Sinopharm) and RhB (99.0% purity, Fuchen) were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. and used without further purification. $PbMoO_4$ crystals with polyhedral shape were prepared by microemulsion-assisted solvothermal method. A quaternary reverse microemulsion, CTAB/water/n-octane/n-butanol, was selected for this study. In a typical synthesis, two identical solutions were prepared by dissolving CTAB (2 g) in 40 mL of n-octane and 10 mL of n-butanol which were stirred for 30 min. After that, 5 mL of 0.2 M Na_2MoO_4 aqueous solution and 5 mL mixed aqueous solutions including 2.5 mL $Pb(AC)_2$ (0.4 M) and 2.5 mL NTA (0.4 M) were added to the solutions, respectively. The two obtained solutions were mixed and stirred for another 30 min to form transparent microemulsion solutions. Then the mixture was sealed in a Teflon-lined stainless-steel autoclave of 130 mL capacity. The tank was heated to and maintained at 160 °C for different times (1 h, 5 h, and 10 h, respectively) and then allowed to cool to room temperature. The resulting products were separated by centrifugation, washed with deionized water and absolute ethanol several times and dried at 80 °C for 4 h.

2.2. Characterization

The overall crystallinity of the as-synthesized $PbMoO_4$ samples were analyzed by X-ray diffraction (XRD) with monochromatized Cu Kα incident radiation ($\lambda = 1.5418$ Å) by a Shimadzu XRD-7000 operated at 40 kV voltage and 30 mA. XRD patterns were recorded from 20° to 60° (2θ) with a scanning rate of 4° min^{-1}. The morphology of the $PbMoO_4$ products was characterized by field emission scanning electron microscopy (FESEM, S-4800) operated at an acceleration voltage of 5 kV. The micro-Raman (MR) spectra of the products were obtained with a Raman spectrometer (LabRAM ARAMIS) with a radiation of 532 nm from an argon ion laser. Photoluminescence (PL) spectra were examined using a fluorescence spectrophotometer (Fluorolog-Tau-3, USA) with Xe lamp (power: 350 W) as the light source at room temperature.

2.3. Photocatalytic activity measurements

The photocatalytic activities of the $PbMoO_4$ samples were evaluated by the degradation of RhB under UV light irradiation ($\lambda = 254$ nm). UV light was obtained by a 12 W Hg lamp (the Institute of Electric Light Sources, Beijing) at room temperature. The photocatalytic reaction was carried out with 0.1 g of powder photocatalysts suspended 100 mL of RhB solution (1×10^{-5} mol/L) in a glass cell. The mixture was sonicated (ultrasound frequency: 40 KHz, Kun Shan) before illumination and stored in the dark for a further 30 min to obtain the saturated absorption of RhB onto the catalysts. 3 mL aliquot was taken at 15 min intervals during the experiment and centrifuged to remove the particles. The filtrates were analyzed by recording the variations of the absorption band maximum (553 nm) in the UV–visible spectrum of RhB using a UV-2100 spectrophotometer (Unico, USA).

3. Results and discussion

Fig. 1(a) shows the typical XRD patterns of $PbMoO_4$ samples obtained via NTA assisted microemulsion-based solvothermal method under different reaction times. All the diffraction peaks can be indexed by a body-centered tetragonal phase of scheelite structure with lattice constants $a = 5.433$ Å and $c = 12.11$ Å, which is in agreement with the literature value (JCPDS No. 77-0431). The strong and sharp peaks indicate the high crystallinity of $PbMoO_4$. EDX measurement made on the $PbMoO_4$ sample prepared with 10 h indicates that the sample is composed only of Pb, Mo, and O elements as shown in Fig. 1(b). EDX analysis also demonstrates that the composition within the experimental error is consistent with the stoichiometry of $PbMoO_4$, which is consistent with the results of the XRD patterns. Fig. 1(c) shows the Raman spectra of the $PbMoO_4$ sample. The Raman peak at 871.4 cm^{-1} was assigned to the symmetric stretching vibration mode $\nu_1(A_g)$ of the $[MoO_4]$ clusters in the $PbMoO_4$ crystal [20]. The peaks at 768.3 and 745.7 cm^{-1} corresponded to the anti-symmetric stretching $\nu_3(B_g)$ and $\nu_3(E_g)$ vibration modes, respectively. Two modes at 351.5 and 310.0 cm^{-1} were interpreted as the weaker $\nu_4(B_g)$ and stronger $\nu_2(A_g)$ of the regular $[MoO_4]^{2-}$ tetrahedrons. The A_g mode at 169.2 cm^{-1} for $PbMoO_4$ is much weaker than other modes. These results were consistent with other previous reports about $PbMoO_4$ [20,22]. No peaks in the XRD or Raman spectra from other impurities were detected. Therefore, it is reasonable to conclude that well-crystallized $PbMoO_4$ crystals have been successfully synthesized with the microemulsion-based solvothermal method.

Fig. 2 shows the typical FESEM micrographs of as-prepared $PbMoO_4$ crystals obtained with different reaction time. Fig. 2(a) is FESEM micrograph of $PbMoO_4$ crystals prepared with 1 h, from which one can see that the small nanocrystals with size of about 40 nm were obtained. With the reaction time increasing to 5 h, as can be seen form Fig. 2(b), uniform monodispersed crystals with size around 250 nm is almost the exclusive products. These homogeneous crystals were uniform in size and the nearly polyhedral shapes become evident. When the reaction time further prolonged to 10 h, large scale of polyhedral crystals with size of 600 nm were obtained, as shown in Fig. 2(c). Fig. 2(d) is a high magnification FESEM micrograph of the crystals, from which we can clearly see that

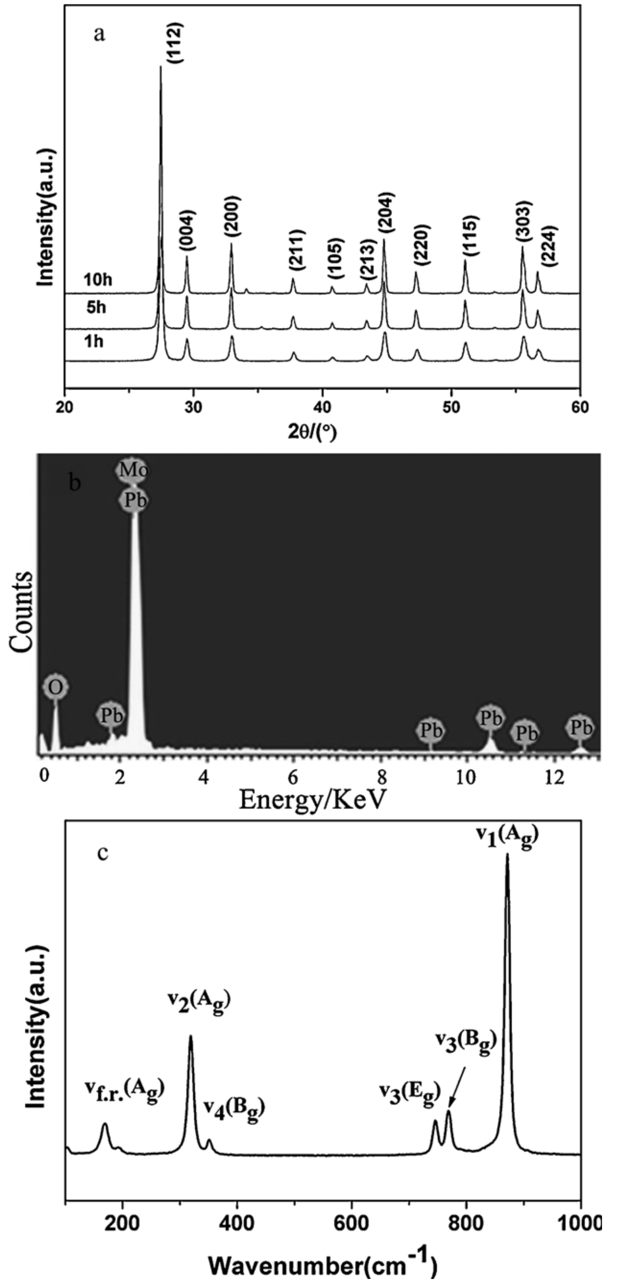

Fig. 1. (a) XRD patterns of $PbMoO_4$ crystals; (b) EDX of the $PbMoO_4$ product, further confirming the element composition of the product; (c) Raman spectra of the $PbMoO_4$ crystals.

crystals possess the shape of polyhedron with well-defined face contour. Careful observation of inset of Fig. 2(d), a high magnification FESEM micrograph of an individual polyhedral crystal, indicates that the crystal is in the shape of regular 18-facet polyhedron with well-defined faces along the different crystallographic planes. According to literature [20], the 18-facet polyhedron exhibits two {0 0 1} faces, eight {1 0 1} faces and eight {1 1 1} faces. The surfaces of the crystals are extremely smooth without any small particles attached on them.

The comparison experiments show that the addition of NTA in the reaction system has a significant effect on the formation of well-defined and uniform $PbMoO_4$ polyhedral crystals. Fig. 3 shows the $PbMoO_4$ samples prepared without the addition of NTA to the microemulsion system. When the reaction time is about 1 h, it can be seen from Fig. 3(a) that tiny nanoparticles were also obtained, similar with Fig. 2(a). While the reaction time is prolonged to 5 h and 10 h, from Fig. 3(b and c), we can clearly see that the crystals were not in the homogenous shape of 18-facet polyhedron and its sizes were not uniform. It is known that Pb^{2+} ions and CTAB in aqueous solutions can form complex easily and thus homogenous and transparent microemulsion solutions are difficult to obtain. When NTA aqueous solutions were added to Pb^{2+} aqueous solutions, NTA can react with Pb^{2+} ions as complexing agent to form Pb–NTA complex and thus avoiding the reaction of Pb^{2+} and CTAB [23]. Therefore homogenous microemulsion solutions can be achieved and the reaction of Pb–NTA complex and $MoO_4{}^{2-}$ ions can be carried out within the microreactors of microemulsion and then uniform $PbMoO_4$ polyhedron crystals can be obtained. The reaction process can be expressed by Eqs. (1) and (2) [23]:

$$3Pb^{2+} + 2NTA^{3-} \rightarrow 3Pb^{2+} - 2NTA^{3-} \tag{1}$$

$$\begin{aligned} &3Pb^{2+} - 2NTA^{3-} + 3H^{+} + 3MoO_4{}^{2-} \\ &\quad \rightarrow PbMoO_{4(s)} \downarrow + 2NTA^{3-} + 3H^{+} \end{aligned} \tag{2}$$

The room temperature PL spectra of the $PbMoO_4$ samples prepared via the microemulsion-based solvothermal method in the presence of NTA were shown in Fig. 4, which were investigated at an excitation wavelength of 300 nm and measured from 400 to 600 nm. It is clear that the $PbMoO_4$ samples prepared with different reaction times exhibit similar emission peaks corresponding to the blue emission, which was consistent with previous reports [20,22]. However, there is a remarkable change of the absolute luminescence intensity for these $PbMoO_4$ crystals prepared with different times. The emission intensity of $PbMoO_4$ polyhedrons (prepared with 10 h) is much stronger than that of samples with 1 h and 5 h. These results indicate that the PL intensity depends strongly on morphology and crystallinity of the crystals. The emission spectrum of the metal molybdates might be ascribed to the charge-transfer transitions within the $[MoO_4]$ clusters [25]. During the excitation process at room temperature, the electrons situated at lower intermediary energy levels (oxygen 2*p* states) absorb the photon energies ($h\nu$) arising from 300 nm (≈4.14 eV) wavelength. As consequence of this phenomenon, the energetic electrons are promoted to higher intermediary energy levels (molybdenum 5*d* states) located near the conduction band. When the electrons fall back to lower energy states again via radiative return processes, the energies arising from this electronic transition are converted in photons ($h\nu'$). In this case, the several photons ($h\nu'$) originated by the participation of different energy states during the electronic transitions are responsible for the broad PL spectra [25].

As a widely used dye, RhB was selected as a representative pollutant to evaluate the photocatalytic efficiency of the as-prepared $PbMoO_4$ polyhedral crystals. The characteristic absorption band of RhB is at about 553 nm, which is employed

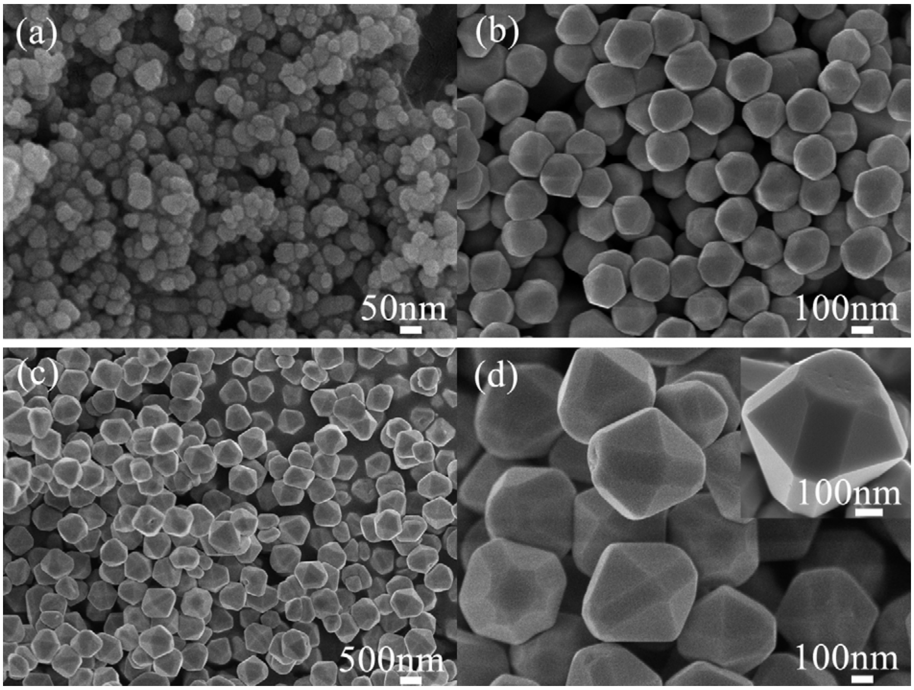

Fig. 2. FESEM micrographs of $PbMoO_4$ crystals prepared with different reaction times via NTA assisted microemulsion-based solvothermal method: (a) 1 h, (b) 5 h, and (c and d) 10 h.

to monitor the photocatalytic degradation of RhB [24]. Fig. 5 reveals the temporal evolution of the absorption spectra of an RhB aqueous solution catalyzed by the $PbMoO_4$ polyhedral crystals under ultraviolet-visible light irradiation. The absorption of the dye solution decreased gradually under ultraviolet-visible light irradiation and the major absorption peak shifted to shorter wavelengths of about 528 nm step by step, indicating the degradation of the dye and the removal of ethyl groups. In addition, the color of the dye solution changes from initial pink to light pink, then to transparent, revealing the complete photocatalytic decolorization of RhB aqueous solution after 120 min irradiation with ultraviolet-visible light. Based on the above result, it can be concluded that $PbMoO_4$ uniform polyhedral crystals display excellent photocatalytic activity for the decomposition of RhB under ultraviolet-visible light irradiation.

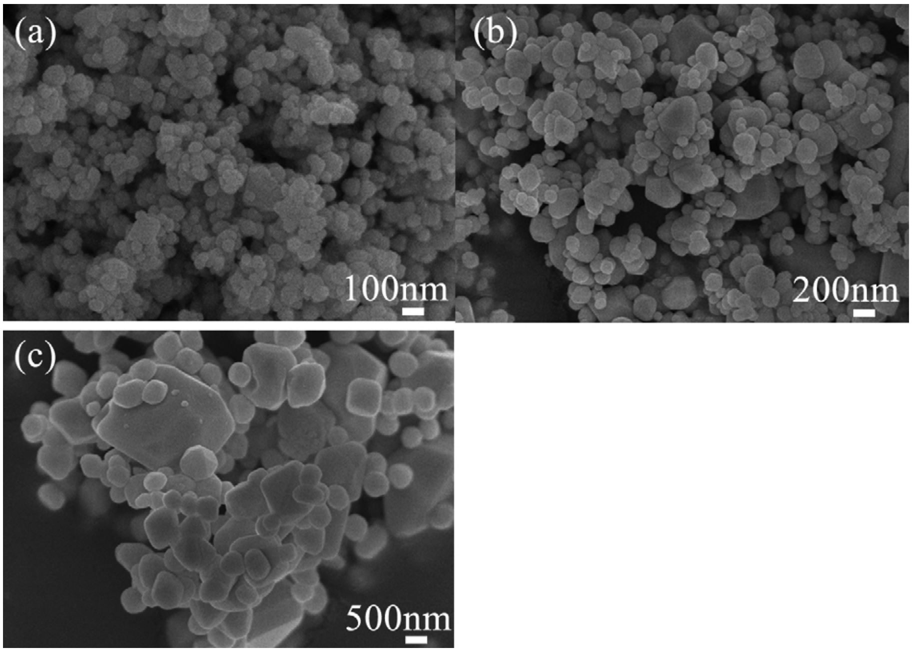

Fig. 3. FESEM micrographs of $PbMoO_4$ crystals prepared without NTA: (a) 1 h, (b) 5 h, and (c) 10 h.

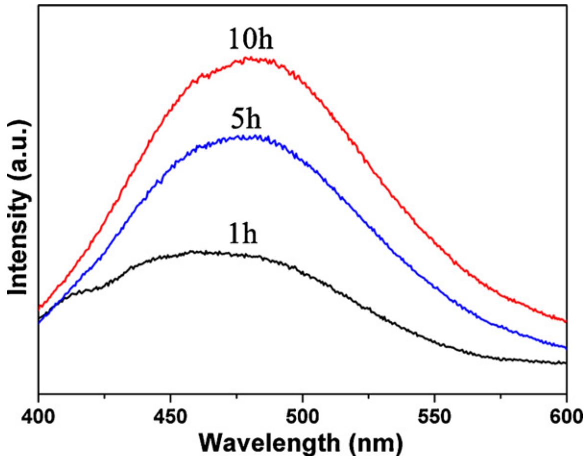

Fig. 4. PL spectra at room temperature of the $PbMoO_4$ crystals prepared with different reaction times.

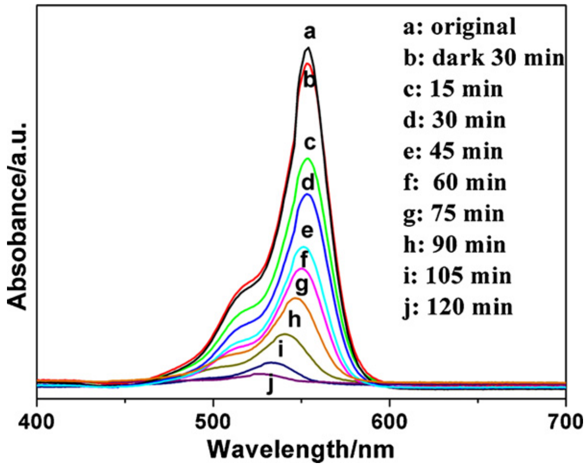

Fig. 5. Temporal evolution of the absorption spectra of the RhB solution in the presence of $PbMoO_4$ polyhedral crystals under UV–visible light irradiation.

4. Conclusions

In summary, we have obtained uniform $PbMoO_4$ crystals with polyhedral shape via a microemulsion-based solvothermal method in the presence of complexing reagent NTA. The addition of NTA into the reaction system leads to formation of Pb–NTA complex and thus homogenous microemulsion solutions, which plays an important role in the formation of homogenous $PbMoO_4$ polyhedral crystals. The polyhedrons prepared at 160 °C with 10 h are in the shape of regular 18-facet polyhedron with well-defined face contour. The as-prepared $PbMoO_4$ polyhedral crystals show an intense blue PL emission at room temperature under the 300 nm wavelength excitation, which is mainly attributed to the charge-transfer transitions. The $PbMoO_4$ polyhedrons are displayed to possess superior photocatalytic activity in the photodegradation of RhB under UV–visible light irradiation. Furthermore, this simple and mild method also presents a way for the synthesis of other homogeneous crystals.

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