



Morphology and photoluminescence of BaMoO₄ micro- and nano-crystals synthesized by coprecipitation method

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Abstract: Barium molybdate (BaMoO₄) micro- and nano-crystals were synthesized by the coprecipitation method. Utilizing the water as the solvent provides octahedron-like nanostructures. These nano-crystals were structurally characterized by X-ray diffraction, energy dispersive X-ray micro-analysis, Fourier transform infrared spectra. The size and shape were observed by scanning electron microscopy. The optical properties were studied by ultraviolet–visible diffuse reflectance spectroscopy and photoluminescence measurements at room temperature. The effects of temperature, solvent, surfactant and barium source were considered to obtain a controlled shape. It is found that the morphology, particle size and phase of the final products are extremely affected by these parameters.

Key words: BaMoO₄; microcrystals; nanocrystals; coprecipitation; photoluminescence

1 Introduction

The molybdates have fascinated much consideration because of their particular luminescence and structure originated from the MoO₄²⁻ group [1,2]. Among the molybdate oxides with scheelite-type tetragonal structure, such as AMoO₄ (A=Sr²⁺, Ca²⁺, Pb²⁺ and Cd²⁺), BaMoO₄ is a significant material, so that many studies have been performed on the synthesis technique and optical properties of BaMoO₄ [3–10]. A current tendency in material synthesis is to investigate new methods to control the architecture and morphology at all dimensions from the nanoscale to macroscopic scale.

Diverse methods have been explored to synthesize these materials, involving solid-state reaction [11], electrochemical method [12], combustion synthesis [13], reverse microemulsion process [14], complex polymerization [15], solvothermal synthesis [16], molten salt route [17] and microwave-assisted citrate complex method [18]. Among all these approaches, the coprecipitation process has demonstrated to be an effective approach to synthesize inorganic nanomaterials with interesting morphologies and regular particle

sizes [19–26].

In this work, a new coprecipitation approach was proposed to synthesize homogeneous octahedron-like BaMoO₄ nanostructures. Furthermore, the morphology of BaMoO₄ nanostructures can be regulated by adjusting the processing parameters.

The reaction was proceeded in an open system at atmospheric pressure. No other additives were utilized. This method has apparent advantages like easy experimental set-up, easy handling, short reaction time, environmental friendliness, and the process is very simple, fascinating and novel by focusing large amount of coprecipitation into the solutions to manufacture pure products. To the best of our knowledge, no such studies have ever been reported.

2 Experimental

2.1 Synthesis of octahedron-like BaMoO₄ nanostructures

BaMoO₄ nanostructures were prepared by a simple coprecipitation method. In a typical procedure, an aqueous solution of Ba(Sal)₂ (Sal=salicylidene) in the presence of different surfactants, such as poly vinyl

pyrrolidone (PVP), sodium dodecyl sulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB), was mixed with $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ aqueous solution and the mixed solution was heated up to 70 °C for 2 h. The white precipitate was centrifuged, washed with distilled water and methanol three times and dried under vacuum at 60 °C. The effects of temperature, solvent, surfactant and barium source on the morphology and particle sizes of BaMoO_4 nanostructures were investigated.

2.2 Synthesis of $\text{Ba}(\text{Sal})_2$ complex

$[\text{Ba}(\text{Sal})_2]$ was synthesized as follows: 2 mmol barium(II) nitrate $[\text{Ba}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$ was dissolved in 40 mL distilled water, a solution of 4 mmol salicylaldehyde dissolved in the same volume of methanol was dropwise added to the above solution under magnetic stirring. After the addition of all reagents, the mixture was refluxed for about 3 h.

2.3 Materials and experiments

All the chemicals were of analytical grade and purchased from Merck and used as-received without further purification. X-ray diffraction (XRD) patterns were recorded by a Rigaku D-max C III X-ray diffractometer using Ni-filtered CuK_α radiation. Scanning electron microscopy (SEM) images were obtained on a Philips XL-30ESEM scanning electron microscope equipped with an energy dispersive X-ray spectroscopy (EDX). Fourier transform infrared spectroscopy (FT-IR) was recorded with a Shimadzu Varian 4300 spectrophotometer in KBr pellets. EDS analysis was performed on a Philips EM208 energy dispersive spectrometer. Room temperature photoluminescence (PL) was studied on a PerkinElmer (LS 55) fluorescence spectrophotometer. Transmission electron microscopy (TEM) images were obtained on a JEM-2100 transmission electron microscope with an accelerating voltage of 200 kV.

3 Results and discussions

3.1 XRD analyses

The crystal structure and composition of the as-prepared products were determined by XRD. The XRD patterns of the barium molybdates obtained under different conditions (surfactant) are presented in Fig. 1. All peaks in Fig. 1 correspond to the reflections of tetragonal phase of BaMoO_4 , which are in a good agreement with the reported data (JCPDS: 08-0455). No remarkable diffractions of other phases can be found in the XRD patterns, exhibiting that a pure BaMoO_4 phase forms.

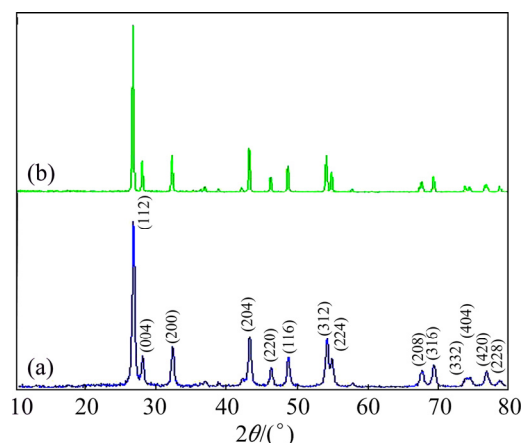


Fig. 1 XRD patterns of BaMoO_4 nanostructures obtained in presence of SDS and methanol (a), and CTAB and water (b) at 30 °C

3.2 FT-IR analyses

Figure 2 shows the FT-IR spectra of $\text{Ba}(\text{Sal})_2$ precursor and BaMoO_4 nanostructures. The vibrations of BaMoO_4 are sorted into the internal and external modes [27]. The first belongs to the vibration inside $[\text{MoO}_4]^{2-}$ units. Their centers of masses are stationary. The second is called lattice phonon mode which corresponds to the motion of Ba^{2+} cations and the rigid molecular units [27–29]. Figure 2(a) exhibits the FT-IR spectrum of BaMoO_4 nanostructures acquired in methanol as the solvent and SDS as the surfactant. The spectrum illustrates a band of Mo—O stretching vibration in tetrahedral MoO_4^{2-} clusters [15] at 791–900 cm^{-1} . It is one of the internal modes indicated as antisymmetric stretching vibrations [15] of the three products. Weak Mo—O bending vibrations [28] are also discerned at about 403 cm^{-1} for BaMoO_4 nanostructures. In the case of $[\text{Ba}(\text{Sal})_2]$ (Fig. 2(b)), the peaks at 1525 and 1639 cm^{-1} belong to the C—O stretching vibrations ($\nu_{\text{C-O}}$) and the peak at 1436 cm^{-1} belongs to C—C stretching vibrations ($\nu_{\text{C-C}}$) of the salicylaldehyde. Free

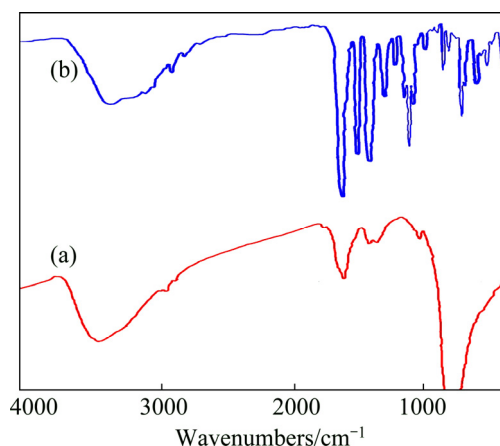


Fig. 2 FT-IR spectra of BaMoO_4 (a) and $\text{Ba}(\text{Sal})_2$ (b) obtained in presence of SDS and methanol at 30 °C

salicylaldehyde $\nu_{\text{C-O}}$ emerges at 1680 and 1660 cm^{-1} , and $\nu_{\text{C-C}}$ emerges at 1490 and 1380 cm^{-1} . Upon complex formation, these stretching vibrations shift to lower regions. The broad absorption band nearby 3332 cm^{-1} in Fig. 2(a) is appointed to the stretching vibrations of absorbed water. The absorption peaks at 469–939 cm^{-1} belong to Ba—O band, there are no absorption bands nearby this range in salicylaldehyde.

3.3 EDX analysis

EDX analysis was employed to investigate the chemical composition and purity of as-synthesized BaMoO_4 nanostructures. The EDX pattern of BaMoO_4 shown in Fig. 3 exhibits that the only existing elements are Ba, Mo and O. No peak of any impurity is observed, indicating the high purity of the product.

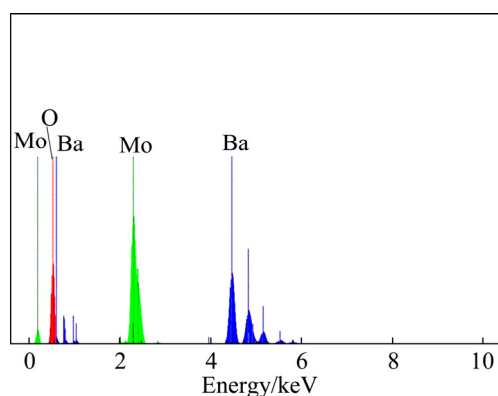


Fig. 3 EDX pattern of BaMoO_4

3.4 SEM images

The morphologies of the samples were investigated by SEM. To explore the effect of surfactant on the morphology of the products, the reaction was performed in the presence of three different surfactants in methanol at 30 °C for 2 h. The SEM images of the samples obtained in the presence of CTAB, PVP and SDS are displayed obtained in Figs. 4(a)–(c), respectively. Figure 4(a) exhibits rod-like nanostructures in the presence of CTAB as the surfactant. In the presence of PVP and SDS as the surfactants, only particle nanostructures form (Figs. 4(b) and (c)).

Figure 5 shows the SEM images of the samples synthesized at 30 °C for 2 h with different solvents via the coprecipitation method. In the presence of propylene glycol (PG) as the solvent, rod-like nanostructures are shaped (Fig. 5(a)). The morphology of as-prepared products changes to octahedron-like nanostructures, when water is utilized as the solvent, as exhibited in Fig. 5(b). Probably, the reason is that the PG is more polar agent than water and can protect the as-formed nuclei in three dimensions and restrict them from further growing in one direction and hinder the formation of octahedron-like nanostructures.

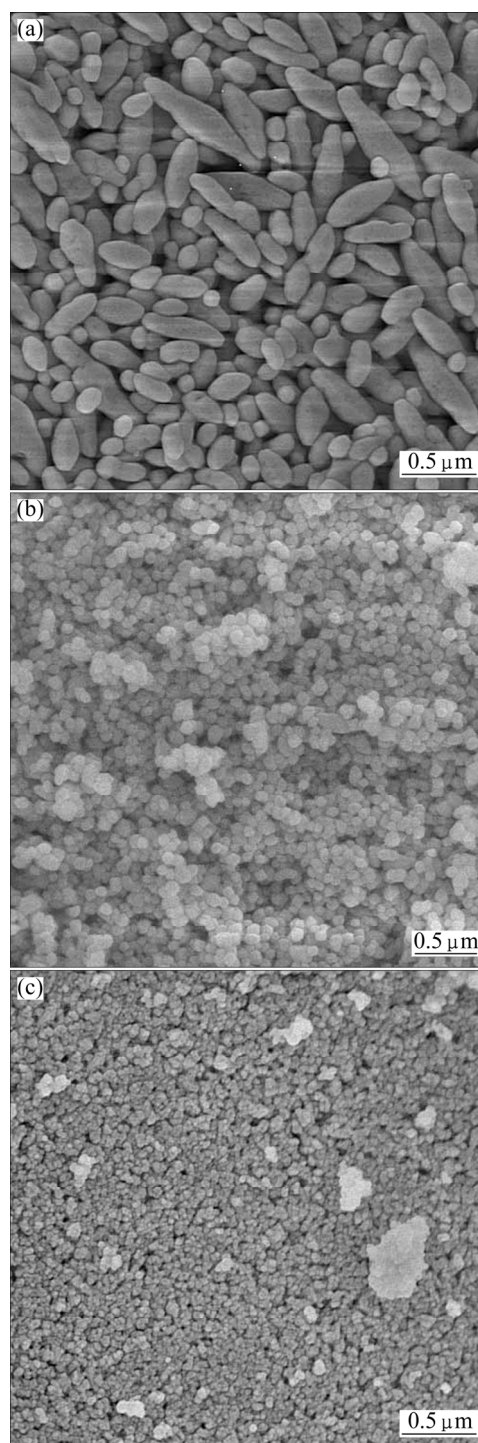


Fig. 4 SEM images of BaMoO_4 obtained from $\text{Ba}(\text{Sal})_2$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in methanol via coprecipitation method in presence of CTAB (a), PVP (b) and SDS (c) as surfactant

Figure 6 shows the SEM images of the samples obtained at 30, 50 and 70 °C. It can be observed that with increasing the reaction temperature from 30 to 70 °C, the size of the nanostructures and their agglomeration enlarge.

The effect of the Ba source on the morphology of BaMoO_4 nanostructures was explored (Fig. 7). Here,

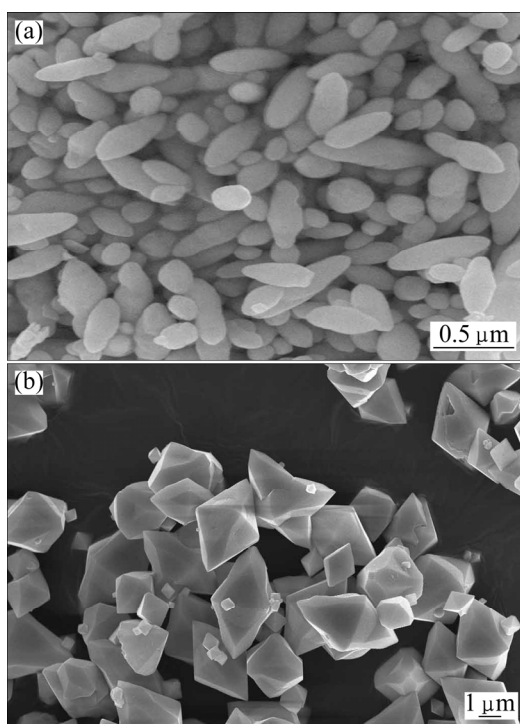


Fig. 5 SEM images of BaMoO₄ obtained from Ba(Sal)₂ and (NH₄)₆Mo₇O₂₄·4H₂O via coprecipitation method with PG (a) and H₂O (b) as solvents

Ba(NO₃)₂ is used as the Ba source and other reaction parameters remain unchanged. Plate-like barium molybdate nanostructures are obtained from Ba(NO₃)₂ salt, as shown in Fig. 7. Figure 8 exhibits octahedron-like barium molybdate nanostructures obtained in the presence of CTAB as the surfactant and water as the solvent. It is proved that water as solvent has critical role for the formation of octahedron-like barium molybdate nanostructures.

3.5 TEM images

Figure 9 shows the TEM images and SAED pattern of BaMoO₄ nanostructures obtained in the presence of SDS and methanol at 30 °C. The obtained TEM images show exhibit that BaMoO₄ nanostructures with an average size of 20 nm and particle-like shape are obtained. The ring-like SAED pattern illustrates that the nanostructures are polycrystalline.

3.6 Optical properties

Figure 10 shows the $(\alpha h\nu)^2$ versus $h\nu$ curve of BaMoO₄ nanostructures which was calculated from their UV–visible absorbance using the equation proposed by THONGTEM et al [29]:

$$\alpha h\nu = (h\nu - E_g)^n \quad (1)$$

where α is the absorbance, h is the Planck constant, ν is the photon frequency, E_g is the energy gap and n is the

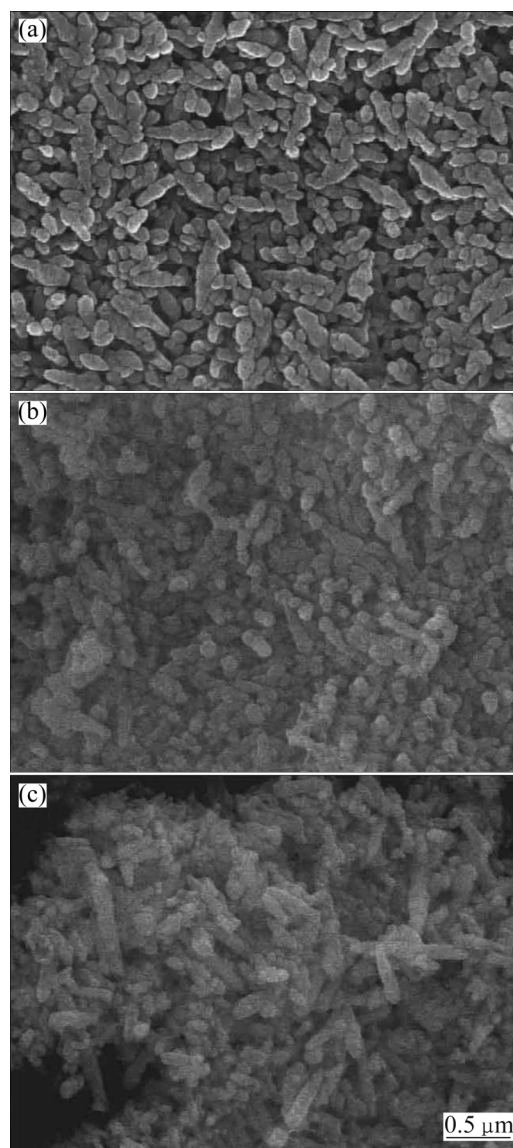


Fig. 6 SEM images of BaMoO₄ obtained from Ba(Sal)₂ and (NH₄)₆Mo₇O₂₄·4H₂O in methanol via coprecipitation method at 30 °C (a), 50 °C (b) and 70 °C (c)

pure number associated with different types of electronic transitions. For $n=1/2$, 2, 3/2 and 3, the transitions are directly allowed, indirectly allowed, directly forbidden and indirectly forbidden, respectively. Each energy gap is determined by the extrapolation of each linear portion of the curves to $\alpha=0$. In the current investigation, the BaMoO₄ presents directly allowed electronic transition ($n=1/2$) [29], and the energy gaps of BaMoO₄ nanostructures is 4.27 eV.

The photoluminescence properties of the prepared BaMoO₄ nanostructures excited at 275 nm at room temperature are shown in Fig. 11. The emission spectra of the metal molybdates are principally due to the charge-transfer transitions within the [MoO₄]²⁻ complex [30]. With the excitation at 275 nm, BaMoO₄

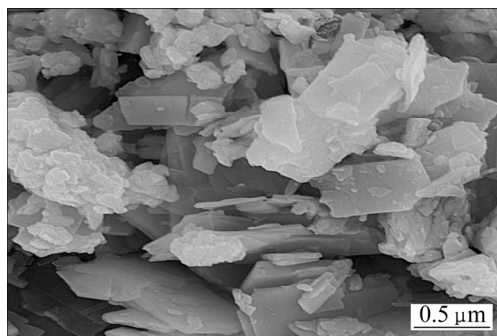


Fig. 7 BaMoO₄ nanostructures obtained from Ba(NO₃)₂ and (NH₄)₆Mo₇O₂₄·4H₂O

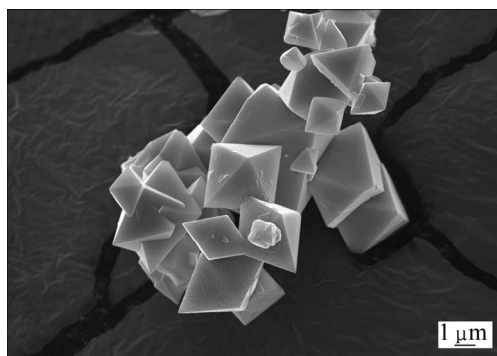


Fig. 8 Octahedron-like BaMoO₄ nanostructures obtained in presence of CTAB and water at 30 °C

nanostructures reveal PL emission in the wavelength of 303 nm (Fig. 11). It is usually accepted that the emission spectra of the barium molybdates are mostly influenced by charged transitions in the [MoO₄]²⁻ complexes, involving some factors such as the distortions of [MoO₄]²⁻ tetrahedron groups happened by the different angles of O—Mo—O, particle sizes, crystalline degree, morphology and surface defects [29].

4 Conclusions

1) Octahedron-like BaMoO₄ nanostructure was successfully synthesized from Ba(Sal)₂ and ammonium hepta molybdate using a simple coprecipitation method at low temperature and pressure.

2) The coprecipitation method has apparent advantages like easy experimental set-up, easy handling, short reaction time, environmental friendliness, and the process is very simple, fascinating and novel by focusing large amount of coprecipitation into the solutions to manufacture pure products.

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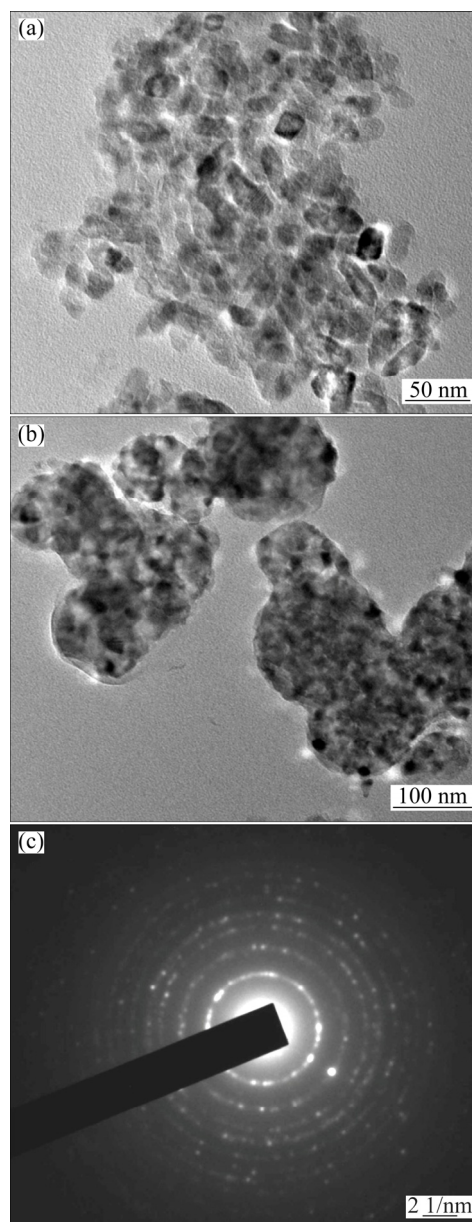


Fig. 9 TEM images (a, b) and SAED pattern (c) of BaMoO₄ nanostructures obtained in presence of SDS and methanol at 30 °C

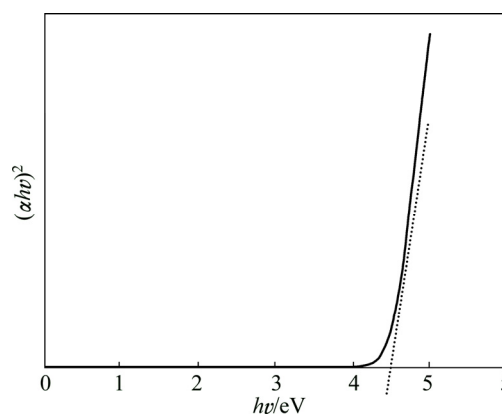


Fig. 10 $(\alpha h\nu)^2$ vs $h\nu$ plot of BaMoO₄ nanostructures obtained in presence of SDS and methanol at 30 °C

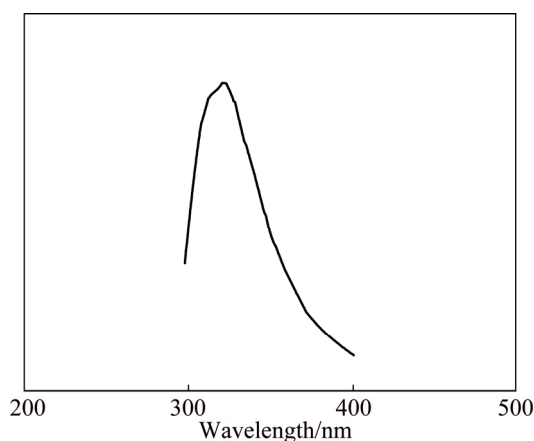


Fig. 11 PL spectrum of BaMoO₄ nanostructures obtained in presence of SDS and methanol at 30 °C

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共沉淀法制备 BaMoO_4 微米和纳米晶的形貌和光致发光

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摘 要: 通过共沉淀法制备钼酸钡(BaMoO_4)微米和纳米晶。采用水作为溶剂可得到八面体状的纳米结构。利用 X 射线衍射、X 射线能谱显微分析和傅里叶变换红外光谱对这些纳米晶结构进行表征, 使用扫描电镜观察其尺寸和形貌, 通过室温下的紫外-可见反射光谱和光致发光测量研究其光学性能。研究温度、溶剂、表面活性剂和钡源对可控形貌的影响, 发现这些参数都极大地影响最终产物的形貌、颗粒尺寸和相。

关键词: BaMoO_4 ; 微米晶; 纳米晶; 共沉淀; 光致发光

(Edited by Mu-lan QIN)