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Short communication

Room temperature synthesis and optical properties of $SrMoO_4$ crystallites by w/o microemulsion

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Abstract

$SrMoO_4$ crystallites with varying morphology have been prepared by the chemical reaction of strontium chloride and sodium molybdate in a reverse microemulsion system consisting of water, OP (*p*-octyl polyethylene glycol phenylether, non-ionic surfactant), 1-pentanol (co-surfactant) and cyclohexane (oil). The resultant powders were characterized in detail by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and photoluminescent spectra techniques (PL), respectively. It was found that $SrMoO_4$ crystallites with different morphologies could be synthesized by the microemulsion process with different aging times. PL spectra showed that the spindle-shape $SrMoO_4$ crystallites with a higher aspect ratio resulted in better photoluminescence property.

Keywords: Strontium molybdate; Water-in-oil microemulsions; Synthesis

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1. Introduction

Recently, metal molybdate/tungstate materials have received much attention owing to their wide application potential in many fields [1–8], e.g. scintillator materials, optical fibers, magnetic materials, and catalysts. The numerous investigations on the synthesis of metal molybdate/tungstate have been carried out, including solvothermal synthesis route to $CaWO_4$ [7], molten salt process for $CdWO_4$ [9], polymer micelle-assisted fabrication of $BaWO_4$ [10], citrate complex method for $BaMoO_4$ [11], sol–gel method for $NiMoO_4$ [12], hydrothermal route to $SrMoO_4$ nanowires [13] and electrochemical preparation of $Ba_{1-x}Sr_x$-MoO_4 films [14].

A microemulsion is an organized and confined reaction medium, in which the size and shape of the resulting particles can be controlled; so microemulsions have been widely used and shown to be powerful as spatially constrained microreactors for controlled synthesis of inorganic crystallites [15,16]. Water-in-oil (w/o) microemulsions have been successfully used to synthesize sulfide semiconductors [17], metal oxides [18], metal particles [19], and some other compounds [20,21] have also been synthesized in such media. Unfortunately, no descriptions concerning the preparation of $SrMoO_4$ powders by the use of water-in-oil microemulsions have appeared. In this paper, for the first time, results on the synthesis of $SrMoO_4$ crystallites in water-in-oil microemulsions are presented. The $SrMoO_4$ crystallites with varying morphology could be synthesized by the microemulsion process with different times aging, while a large $SrMoO_4$ particles (>5 μm in diameter) with an orange-like particle shape was obtained by the direct precipitation method.

2. Experimental procedure

All chemical reagents (strontium chloride ($SrCl_2{\cdot}6H_2O$), sodium molybdate ($Na_2MoO_4{\cdot}2H_2O$), OP ($C_{34}H_{62}O_{11}$), 1-pentanol ($CH_3(CH_2)_4OH$) and cyclohexane (C_6H_{12})) were analytical grade purity, obtained from Shanghai Chemical Reagent Corporation, and used as received without further purification. The water used throughout this work was distilled water.

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Table 1

	M_A	M_B	*V* (ml)
Aqueous phase	0.1 M $SrCl_2 \cdot 6H_2O$	0.1 M $Na_2MoO_4 \cdot 2H_2O$	10
Surfactant	OP	OP	15
Co-surfactant	1-Pentanol	1-Pentanol	10
Oil phase	Cyclohexane	Cyclohexane	70

A typical process is described as follows: two microemulsions (M_A and M_B) with different aqueous phases were obtained (see Table 1). The aqueous phase in the M_A was a 0.1 M solution of $SrCl_2 \cdot 6H_2O$, while 0.1 M $Na_2MoO_4 \cdot 2H_2O$ in M_B. The two microemulsions were mixed together and stirred for 30 min at room temperature. An increased turbidity indicated the formation of the $SrMoO_4$. The resulting white suspension was then aged for 1, 2, 5, 10, and 15 h at room temperature, respectively. Finally, the obtained precipitate was separated by centrifugation, and washed with acetone and absolute ethanol for several times to remove excess OP, and then dried at the room temperature. Yield of the synthesis process was >85.5% after centrifuging and thoroughly washing.

For comparison, $SrMoO_4$ powders were also prepared by a direct precipitation route: appropriate amounts of $SrCl_2 \cdot 6H_2O$ and $Na_2MoO_4 \cdot 2H_2O$ were dissolved in distilled water to form aqueous solutions with 0.1 M concentration, respectively. Then the two solutions were mixed together with strongly magnetic stirring for 30 min at room temperature, and a white precipitate formed. The precipitate aged for a moment, then filtered and washed with distilled water and absolute ethanol for several times, and then dried at room temperature.

Each product was characterized by using an X-ray powder diffractometer (XRD, D/max, Japan) with Cu Kα radiation. The morphology and particle size of the as-prepared powders were observed by using a transmission electron microscope (TEM, JEM-1200EX, Japan), and a scanning electron microscope (SEM, JSM-840, Japan). The room temperature luminescent spectra were recorded on a spectrofluorometer (PL, Fluorolog-3, USA).

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples prepared by the direct precipitation method and microemulsion method, respectively. It indicates that good crystallization of tetragonal phase $SrMoO_4$ can be easily achieved at room temperature. When the aging time was increased from 1 to 5 h, no significant difference was observed in the XRD patterns. All of the XRD patterns are consistent with the reported data (JCPDS: 85-0586), and no other impurities were found.

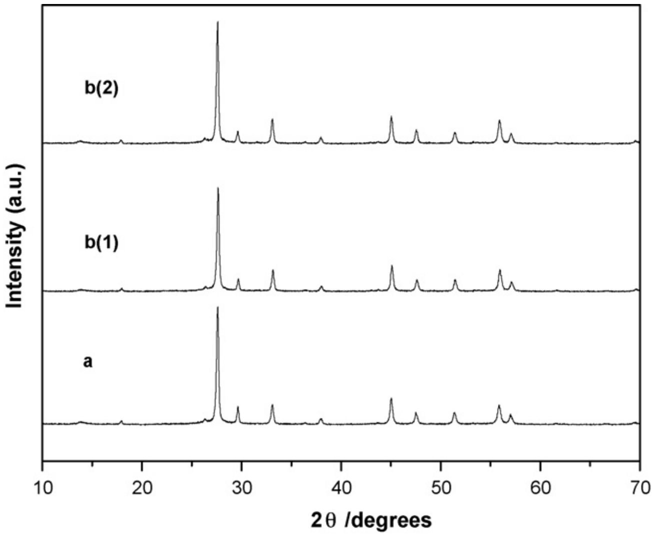

Fig. 1. XRD patterns of the samples obtained at room temperature by (a) the direct precipitation method, and (b) the microemulsion method for aging (b(1)) 1 h and (b(2)) 5 h, respectively.

SEM and TEM images of the $SrMoO_4$ powders obtained from the different methods are shown in Fig. 2. The direct precipitation method led to the formation of $SrMoO_4$ crystallites of larger particle sizes, approximately 5–7 μm in diameter, with a spherical particle shape like an orange (Fig. 2a). Fig. 2b(1)–b(5) present TEM images of the $SrMoO_4$ powders, prepared by the microemulsion method at room temperature for aging 1, 2, 5, 10 and 15 h, respectively. Obviously, the microemulsion method could result in the formation of $SrMoO_4$ crystallites with different morphologies in the same microemulsion system by varying the aging time. As shown in Fig. 2, the morphology of the $SrMoO_4$ crystallites changed from sphere shape of ca. 100 nm in diameter (Fig. 2b(1)) to spindle one with the high aspect ratios ca. 6 (Fig. 2b(2)) when the aging time was increased from 1 to 2 h. On further increasing the aging time to 5 h, no significant change could be found in morphology but the aspect ratio increased to approximately 8 (Fig. 2b(3)). However, when the aging time increased to 10 h, $SrMoO_4$ crystallites gradually changed into much shorter and wider spindle type particles with the aspect ratio of approximately 3 (Fig. 2b(4)). An aging time of 15 h finally resulted in the formation of ‘‘rice’’-like $SrMoO_4$ particles with the aspect ratio of 2 (Fig. 2b(5)). The above results indicate that, aging time plays an important role for varying morphologies of $SrMoO_4$ crystallites in the microemulsion system.

These results seem to be caused by the fact that the $SrMoO_4$ crystallites with smaller particle sizes, prepared by the microemulsion method, were formed in a controlled manner in smaller domains, which could even keep the composition partition to a nanosized level [22]. In contrast, the $SrMoO_4$ crystallites, prepared by the direct precipitation method, crystallized and grew in an uncontrolled manner, easily leading to an extensive growth, which might be the main reason why the resultant powder was of larger particle sizes than that obtained from the microemulsion process.

Room temperature photoluminescence properties of the as-prepared $SrMoO_4$ crystallites were investigated at an excitation wavelength of 330 nm shown in Fig. 3. The PL emission peak position and intensity of $SrMoO_4$ crystallites rely on their morphologies. An isotropic particle morphology as the

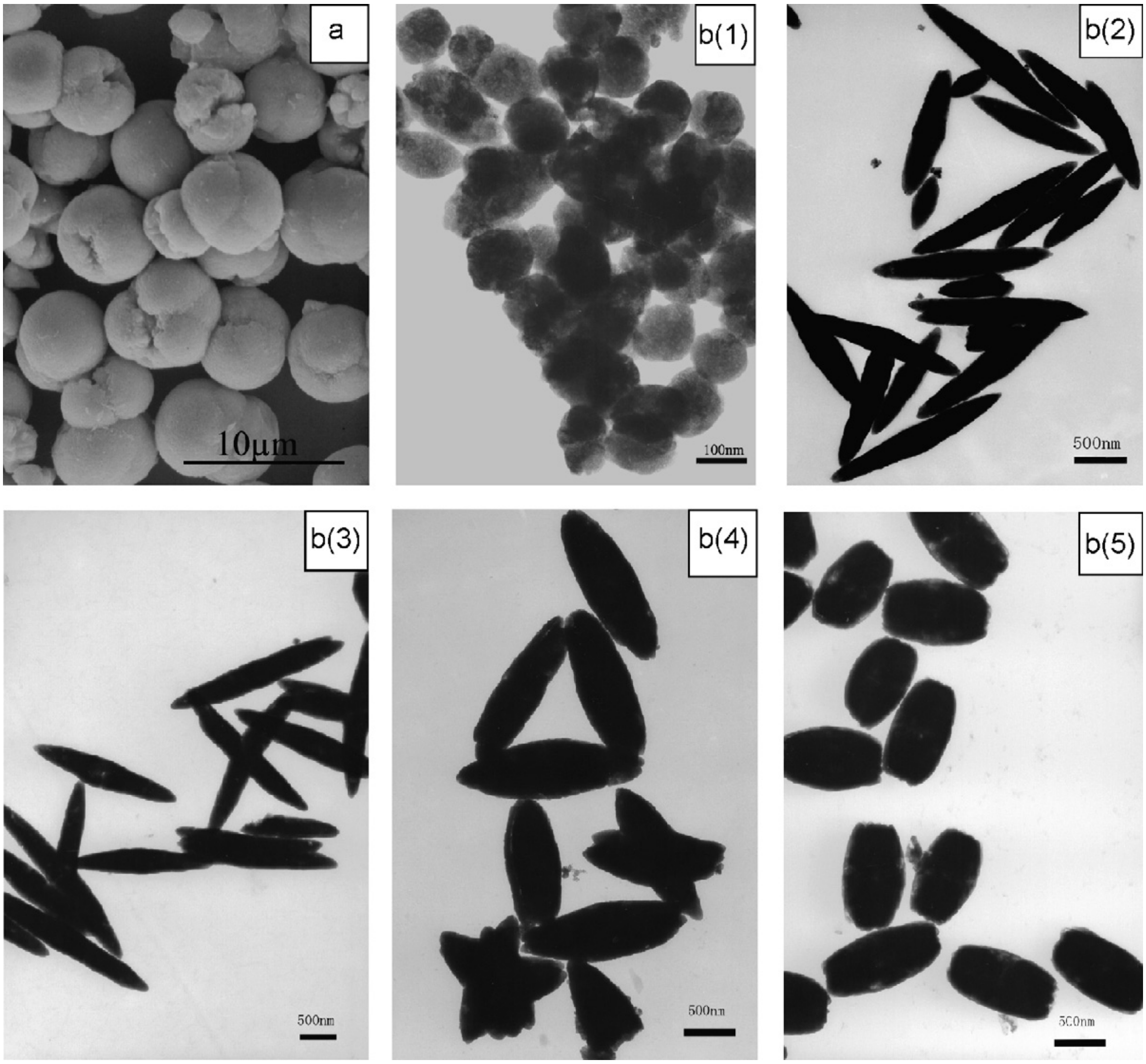

Fig. 2. SEM and TEM images of the $SrMoO_4$ crystallites prepared at room temperature by (a) the direct precipitation method (SEM) and (b) the microemulsion method (TEM) with aging 1 h (b(1)), 2 h (b(2)), 5 h (b(3)), 10 h (b(4)) and 15 h (b(5)), respectively (TEM).

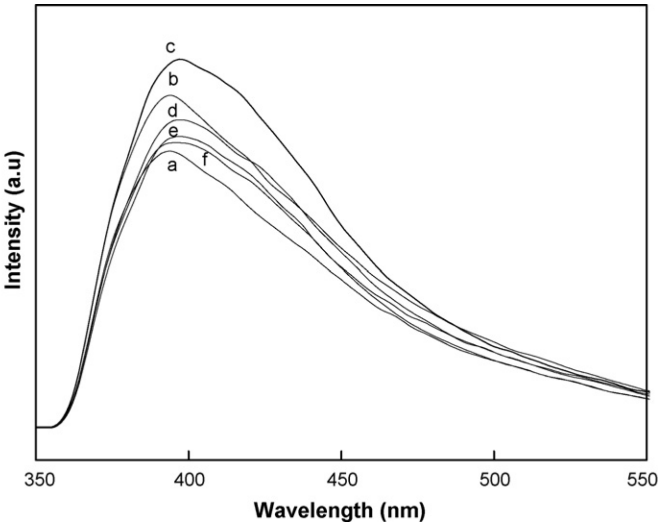

Fig. 3. PL spectra of the $SrMoO_4$ crystallites prepared by the different methods at room temperature: microemulsion method with different aging times (a) 1 h, (b) 2 h, (c) 5 h, (d) 10 h, (e) 15 h; and (f) the direct precipitation method, respectively.

spherical shape (Fig. 2a, Fig. 2b(1)), even when the particle size increased from 100 nm to 5–7 μm, hardly changed the PL emission peak position (390 nm) and its intensity. However, the spindle-shape of $SrMoO_4$ crysitallites**,** prepared by the microemulsion process (aging 2 h), exhibited a slight shift of the emission peak to 394 nm and showed enhancement in PL intensity. Fig. 3a–e presents room temperature PL properties of the as-prepared $SrMoO_4$ samples by the microemulsion method with different morphologies, arising from different aging times. The spherical shape sample with aging time of 1 h (Fig. 2b(1)) exhibits the lowest PL intensity (Fig. 3a). When increasing the aging time to 2 h, the morphology could be changed from sphere to spindle-shape (Fig. 2b(2)), which would obviously increase the PL intensity (Fig. 3b). Further increasing the aging time to 5, 10 and 15 h, the strongest PL intensity of $SrMoO_4$ sample appeared at the aging time of 5 h (Fig. 3c), corresponding to a maximal aspect ratio. It implies that the PL emission intensity of $SrMoO_4$ crystallites is affected by their morphology and aspect ratio.

4. Conclusions

$SrMoO_4$ crystallites with different morphologies could be successfully prepared by a microemulsion method, while the direct precipitation method resulted in larger spherical particles due to the uncontrolled crystallization and extensive growth of $SrMoO_4$ crystallites. The $SrMoO_4$ crystallites with various morphologies show a different PL performance. The spindle-shape $SrMoO_4$ crystallites with a higher aspect ratio exhibit a great photoluminescence intensity.

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