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# Synthesis of $BaMoO_4$ hollow spheres

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**Abstract** Based on the ''polymer-cation templates'' technique, well-defined $BaMoO_4$ hollow spheres with an average diameter of 2.3 μm have been synthesized via a simple precipitation reaction between $BaCl_2$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ at room temperature in the presence of poly(methacrylic acid). The size of the hollow spheres could be tuned down to 1.5 μm by decreasing the concentrations of $Ba^{2+}$ or $MoO_4^{2-}$ ions in the reaction solution. Compared with current fabrication routines for hollow spheres, this method is facile and cost-effective as no surfactant is needed, and can be applied to produce other inorganic hollow-structured materials.

## Introduction

Inorganic hollow spheres with diameter ranging from nanometer to micronmeter have attracted a great deal of attentions. Due to their core-shell structures, they can be used in various fields, such as controlled release capsules (for medicines, cosmetics, catalysts, etc.), artificial cells, chromatographic separation, and photo-electronic devices [1–5]. Many efforts of preparing these materials are focused on sacrificial templates, involving carbon and polystyrene microspheres, exchange resin spheres, liquid droplets, emulsions and polymer-surfactant micelles [6–10]. Among these works, Qi *et al.* had demonstrated a novel and general polymer-surfactant system for preparing calcium carbonate and silver hollow spheres at ambient condition [9–10]. The polymer used in their approach was poly(ethylene oxid)-*block*-poly(methacylic acid) (PEO-*b*-PMAA), the so-called double hydrophilic block copolymer, and the surfactant being used was sodium dodecylsulfate. Recently, Yu et al. had also obtained calcium carbonate hollow spheres by a polymer-surfactant system using poly(styrene-*alt*-methacrylic acid) (PSMA) and cetyltrimethylammonium bromide [11].

To minimize the fabrication cost and eliminate the need of surfactant, we have developed a method of using a single ploymer system, namely poly(methacrylic acid) (PMAA). It is known that cross-linking is possible during the neutralization process between certain types of cations (M) and polymers such as copolymer of butadiene, acrylonitrile or acrylic acid [12]. In the product, M were captured in the cross-linked polymer macromolecules and served as part of the templates. When utilizing this so-called ''polymer-M templates'' technique to fabricate inorganic hollow structures, the M attached to the ionic cross-links react readily with those free species in the reaction solution. As a result, closed solid shells gradually form around the entire surface of the templates. Based on this proposed mechanism, we had systematically studied the syntheses of a series of semiconducting materials, including $SrWO_4$ [13]. The main objective of the present work is to develop a facile routine for fabricating inorganic hollow spheres. Its importance is not in the synthesis of some specific materials, but in opening a versatile route to fabricate inorganic hollow structures. Our target material is Barium molybdate ($BaMoO_4$) crystal with scheelite structure. It is a photo-electronic material, which has been used

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in solid-state lasers [14, 15]. Recently, $BaMoO_4$ nanobelts and their penniform superstructures have been obtained via the catanionic reverse micelles [16], but so far, there is no report on $BaMoO_4$ hollow structures. Our current work on $BaMoO_4$ is part of a systematic study on the fabrication of inorganic hollow crystals by facile and inexpensive routes. The success of forming $BaMoO_4$ hollow spheres have provided a new example for our designed synthetic route to hollow structures, and more importantly, it adds extra creditability to our proposed mechanism in the formation of these hollow spheres.

## Experimental methods

In a typical preparation of hollow $BaMoO_4$ structures, 5 mL of $BaCl_2$ (0.1 mol $L^{-1}$), 2.5 mL of PMAA (10 g $L^{-1}$) and 37.5 mL of distilled water were mixed, before 5 mL of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.014 mol $L^{-1}$) was slowly added in the solution under vigorous stirring. The pH value of the reaction solution was adjusted to 12 by using NaOH and HCl solutions (5 mol $L^{-1}$). The mixture was sealed and incubated for 12 h at room temperature. Thereafter, white precipitate was collected, washed and rinsed with distilled water and ethanol in ultrasonic bath, before drying in air. The synthetic reactions are proposed as follows:

$$Mo_7O_{24}^{6-} + 8OH^- = 7MoO_4^{2-} + 4H_2O \quad (1)$$

$$MoO_4^{2-} + Ba^{2+} = BaMoO_4 \quad (2)$$

Scanning electron microscopy (SEM) (LEO 1450VP) equipped with energy dispersive x-ray spectrometry (EDS) was used to characterize the morphology and chemical composition of the product. X-ray diffractometry (XRD) with $CuK_\alpha$ (1.5405981 Å) radiation was used to determine the crystalline structure of the product.

## Results and discussion

### XRD and SEM analyses

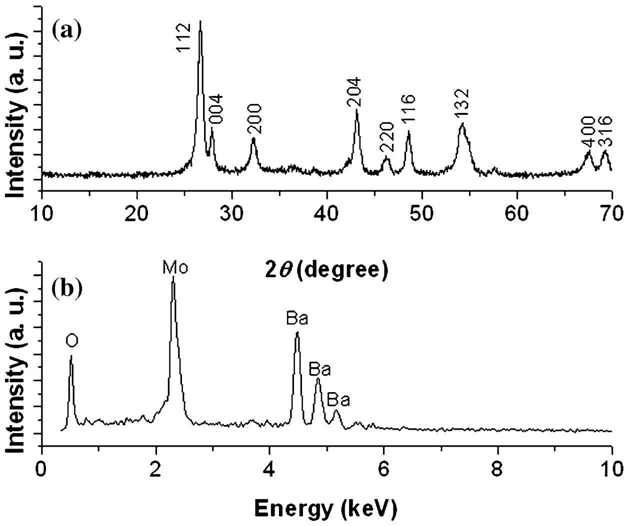

**Fig. 1** (**a**) XRD pattern and (**b**) EDS spectrum of the BaMoO4 product obtained at [PMAA] = 0.5 g $L^{-1}$, $[Ba^{2+}]$ = 0.01 mol $L^{-1}$, $[Mo_7O_{24}^{6-}]$ = 0.00143 mol $L^{-1}$, and pH = 12

The white precipitate was characterized by XRD. Figure 1a is the XRD pattern of the as-prepared product. The JPCDS file # 89-4570 was used to fit this pattern. The peaks were indexed and they beloged to the tetragonal scheelite structured $BaMoO_4$ with lattice parameters $a$ = 5.5479 Å, $c$ = 12.743 Å, and with a space group of $I4_1/a$. Figure 1b shows the EDS spectrum of the product. It revealed that the sample contained Ba, Mo, and O. Based on the $\phi(\rho z)$ method [17], the atomic ratio of Ba:Mo:O was determined to be 1:0.93:4, which was close to the stoichiometric ratio of $BaMoO_4$. The experimental uncertainty of this analysis was less than 10%.

The $BaMoO_4$ precipitate was examined by SEM before and after they were treated in the ultrasonic bath. Before sonication, it was observed that they were completed spheres. After sonfication, many of them had been perforated with small holes on their surfaces as shown in Fig. 2. The average diameter of the spheres was ~2.3 µm. It was

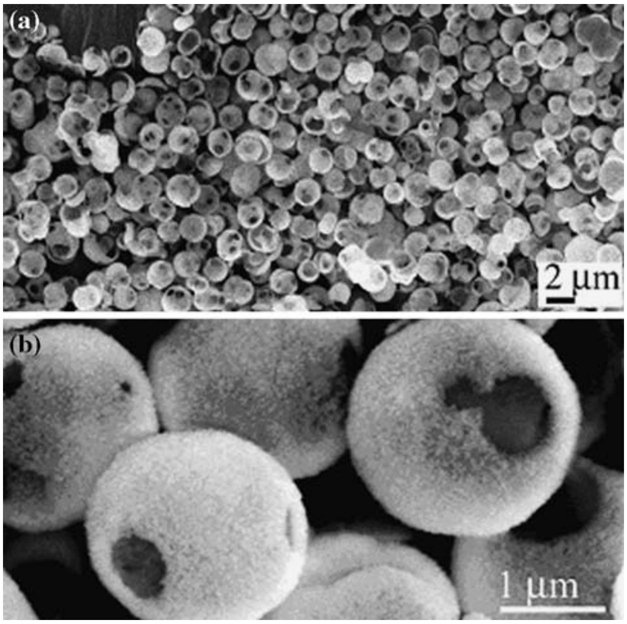

**Fig. 2** (**a**) Low and (**b**) high magnification SEM images of the $BaMoO_4$ spheres. [PMAA] = 0.5 g $L^{-1}$, $[Ba^{2+}]$ = 0.01 mol $L^{-1}$, $[Mo_7O_{24}^{6-}]$ = 0.00143 mol $L^{-1}$, and pH = 12

possible that the spheres were perforated during sonication. The high magnification image of the open spheres in Fig. 2b revealed that they were hollow, and this suggested that the template cores had been removed through these holes during washing and rinsing with water and ethanol in the ultrasonication bath. The SEM also clearly illustrated that these $BaMoO_4$ shells were composed of tiny crystallites. This observation was consistent with the grain size estimation of the product based on the width of the half maximum of the (112) peak in the XRD pattern (Fig. 1a). We calculated that the size of the crystallites composing these shells was about 14 nm.

## Effects of acidity

The formation of PMAA-$Ba^{2+}$ templates was related to the feasibility of the electrostatic interaction between the $COO^-$ radicals of the PMAA marcomolecules and the $Ba^{2+}$ ions. It was reasonable to expect that decreasing the pH value in the reaction solution, i.e. reducing the degree ionization of PMAA, could weaken the electrostatic interaction between PMAA and $Ba^{2+}$, and hindered the formation of the PMAA-$Ba^{2+}$ templates. To verify that electrostatic interaction between PMAA and $Ba^{2+}$ was affected by the acidity of the reaction solution, a controlled experiment was performed by changing the pH value from 12 to 5. In such a case, no $BaMoO_4$ hollow sphere was obtained in the precipitation as shown in Fig. 3a. This indicated that the increased acidity, i.e. lowered degree of ionization of the PMAA, had interrupted the formation of the ‘‘polymer-M templates’’. Thus, the nucleation and growth of the $BaMoO_4$ crystals proceeded without templates and formed bundle-like structures (Fig. 3a).

## Effects of PMAA concentration

The presence of PMAA in the reaction system was essential to the formation of $BaMoO_4$ hollow spheres. To verify this point, another controlled experiment was carried out to prepare preciptation from the $BaCl_2$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ solution mixture without using PMAA. As shown in Fig. 3b, precipitates containing elongated octahedrons were produced under the conditions $[Ba^{2+}] = 0.01$ mol $L^{-1}$, $[Mo_7O_{24}^{6-}] = 0.00143$ mol $L^{-1}$, pH = 12 and [PMAA] = 0. As the concentration of [PMAA] increased, the $BaMoO_4$ particles became larger but with irregular shapes. Figure 4(a, b) shows the $BaMoO_4$ particles obtained from reaction solution with [PMAA] = 0.1 g $L^{-1}$. The SEM images revealed that the surface of the particles were rather rough, and appeared to

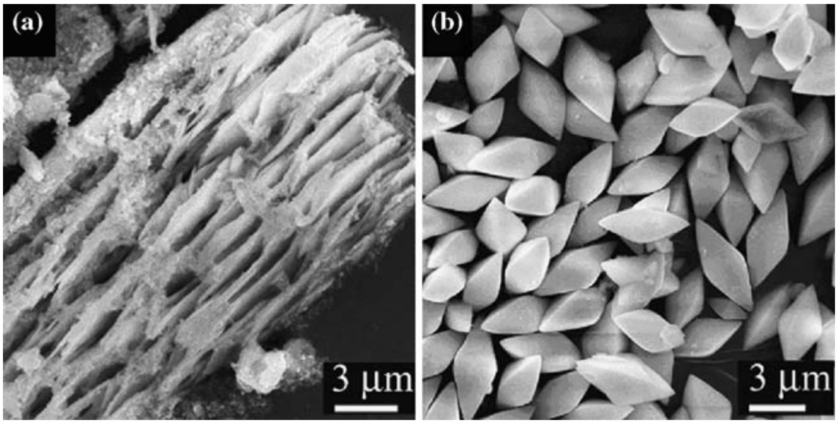

**Fig. 3** SEM images of $BaMoO_4$ products obtained (**a**) pH = 5, and (**b**) [PMAA] = 0. The other parameters were kept the same as stated in the caption of Fig. 2

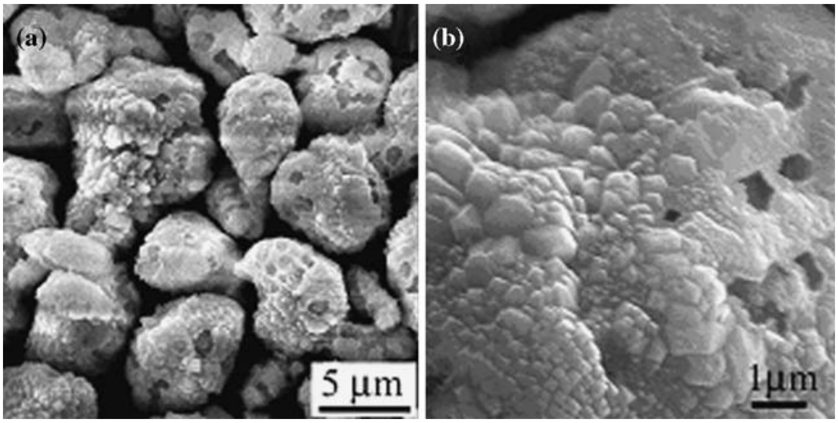

**Fig. 4** (**a**) Low and (**b**) high magnification SEM images of $BaMoO_4$ products obtained at [PMAA] = 0.1 g $L^{-1}$. The other parameters were kept the same as stated in the caption of Fig. 2

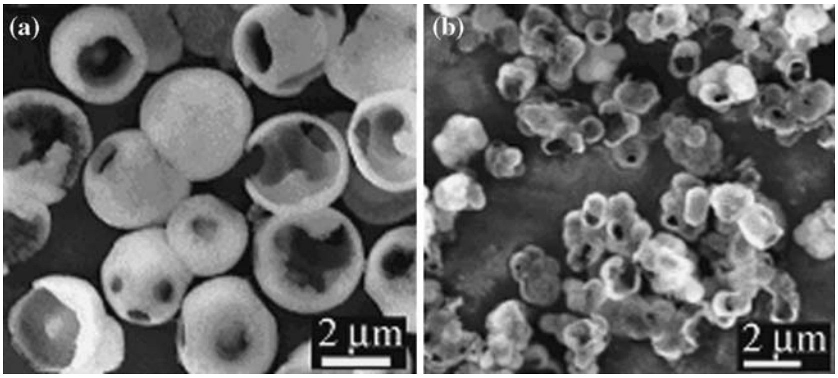

**Fig. 5** SEM images of $BaMoO_4$ products obtained at (**a**) [PMAA] = 0.3 g $L^{-1}$; (**b**) [$Ba^{2+}$] = 0.006 mol $L^{-1}$ and [$Mo_7O_{24}^{6-}$] = 0.00086 mol $L^{-1}$. The other parameters were kept the same as stated in the caption of Fig. 2

be composed of small crystallites. It was possible that each crystallite was formed by nucleation and growth on different individual polymer-M template in the reaction solution. However, due to insufficient free polymer macromolecules which also acted as inhibitors, segregation of $BaMoO_4$ crystallites occurred, and larger $BaMoO_4$ particles with rough surface were produced. In solutions with higher [PMAA] concentrations ranging from 0.3 to 0.9 g $L^{-1}$, uniform-sized $BaMoO_4$ hollow spheres were found. They were of size and appearance similar to those obtained at [PMAA] = 0.5 g $L^{-1}$ (Fig. 5a).

### Effects of barium concentration

It was also found that the size of the $BaMoO_4$ hollow spheres could be changed by varying the concentrations of [$Ba^{2+}$] and [$MoO_4^{2-}$]. When [$Ba^{2+}$] and [$MoO_4^{2-}$] were decreased while keeping [PMAA] = 0.5 g $L^{-1}$ and pH = 12, the hollow spheres became smaller. Fig. 5b shows the $BaMoO_4$ products obtained when [$Ba^{2+}$] = 0.006 mol $L^{-1}$ and [$Mo_7O_{24}^{6-}$] = 0.00086 mol $L^{-1}$. It was observed that smaller $BaMoO_4$ hollow spheres with diameter of ~1.5 µm were obtained. These results could be elucidated with the ‘‘polymer-M templates’’ model. When [$Ba^{2+}$] = 0.01 mol $L^{-1}$, PMAA-$Ba^{2+}$ in situ source templates could be formed in the presence of PMAA having concentration ranged from 0.3 to 0.9 g $L^{-1}$, while the excessive PMAA macromolecules were free, and they acted as inhibitors in the reaction system, and thus uniform-sized $BaMoO_4$ hollow spheres were obtained. Conversely, as $Ba^{2+}$ ions acted as crosslinkers in the PMAA-$Ba^{2+}$ in situ source templates, the decrease of [$Ba^{2+}$] would lead to size reduction of the templates, and eventually resulted in smaller $BaMoO_4$ hollow structures.

## Summary

Using a precipitation reaction between $BaCl_2$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in the presence of PMAA produced well-defined $BaMoO_4$ hollow spheres. Compared with the current polymer-surfactant techniques, this approach is advantageous for its surfactant-free process, and commercial availability and lower price of PMAA over those of PEO-*b*-PMAA or PSMA. Fabrication of $BaMoO_4$, together with our earlier report on the fabrication of hollow $SrWO_4$ and $WO_3$ structures suggests that this facile approach would be generally applied to produce more inorganic materials with hollow structures.

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