

Room-temperature Preparation of BaMoO₄ Nano-octahedra by Microemulsion Method

Yan Mi, Zaiyin Huang,* Zeguang Zhou, Feilong Hu, and Qiufeng Meng

College of Chemistry & Ecological Engineering, Guangxi University for Nationalities, Nanning 530006, P. R. China

(Received November 4, 2008; CL-081039; E-mail: huangzaiyin@gxun.edu.cn)

Uniform barium molybdate nano-octahedra with a mean edge length of 50 nm have been prepared in Triton X-100 water-in-oil (w/o) microemulsions at room temperature. BaMoO₄ nano-octahedra present tetragonal single crystals. The size of these nano-octahedra can be tuned conveniently by changing the reagent concentrations and the molar ratio of water and Triton X-100.

Growth of nanoscale inorganic crystals with uniform shape and size is of fundamental interest and technological importance owing to their unique size- and shape-dependent properties and as potential building blocks for advanced electronic and optoelectronic devices.¹ Great efforts have been devoted to the investigation of effective and efficient methods to obtain fine-tune the shape and size of inorganic crystals in the past few years, such as solution methods,² often assisted by surface surfactant materials, tuning pH values, electrochemical deposition,³ and chemical vapor deposition.⁴

These methods often concentrate on the investigation of tailoring the shape of metals and/or oxides. Scheelite-type alkaline earth molybdates have received much attention in last years owing to their interesting optical and structural properties.⁵ Barium molybdate (BaMoO₄) is one of the most important alkaline earth molybdates, which have potential luminescent and scintillator properties.⁶ However, tuning the shape and size of BaMoO₄ is lacking investigation.⁷ Recently, Cavalcante et al.⁸ reported the obtention micro-octahedrons with average particle size in the range from 0.7 to 3.1 μm of BaMoO₄ by domestic microwave-hydrothermal method. Since nanodevices or nanomachines are built of nanoscale blocks, the preparation of BaMoO₄ in nanometer-size is of both theoretical and practical importance and is still a challenge.

As is well known, the method of water-in-oil microemulsion for the preparation of nanoscale inorganic crystals is a very facile and efficient route. Well-dispersed water pools in w/o microemulsions have been shown to be an ideal microreactor, where ultrafine, uniform, and monodisperse nanoscale inorganic crystals can form.⁹ Herein, we describe a simple solution-phase route to produce uniform BaMoO₄ nano-octahedra with average particle size of 50 nm by a quaternary reverse microemulsion solutions of Triton X-100/*n*-octanol/cyclohexane/water system at room temperature.

In a typical preparation, the quaternary microemulsion was prepared by dissolving Triton X-100 (3.0 g) in 10 mL of cyclohexane and 2.0 mL of *n*-octanol. Each solution was stirred for 30 min and then a certain volume of 0.05 M aqueous BaCl₂ and 0.05 M Na₂MoO₄ solution was added, respectively. The molar ratio of water to Triton X-100 (ω) in each solution was maintained at 10. Another 30 min of stirring was undertaken, resulting in two transparent microemulsions. Equal volumes of

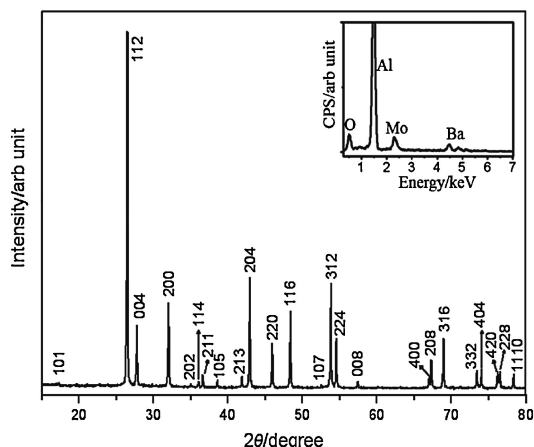


Figure 1. XRD patterns and inset shows EDX spectra for BaMoO₄ nano-octahedra.

the above two microemulsions were mixed slowly and stirred for 5 min. The resulting solution was aged without stirring for 2 days at room temperature. The aged solution was put in a tube and centrifuged at 10000 revolutions/min for 10 min. The transparent solution in the upper part of the tube was removed, followed by addition of acetone and ethanol (volume ratio 1:1), and ultrasonic rinsing for 20 min. This procedure was repeated three times to remove the remaining organics. Pure deionized water and ethanol were subsequently used to rinse these products three times, respectively. Finally, white powder products were obtained after drying in vacuum at room temperature for 12 h.

X-ray diffraction shown in Figure 1 indicates that nano-octahedrons present tetragonal structure free of deleterious phases. BaMoO₄ signs elements O, Al, Mo, and Ba are observed in the energy dispersive X-ray (EDX) spectrometry (see inset Figure 1). Among which Al came from the sample stage, so the sample was composed of O, Mo, and Ba.

Figure 2a shows field emission scanning electron microscopy (FESEM) micrograph of BaMoO₄ nano-octahedrons. High yield of uniform polyhedral crystals with nanometer-size is almost the exclusive products in our synthetic result. The particle size distribution is demonstrated in Figure 2b, acquired by measuring at least 200 particles, which shows a narrow size distribution. A Gaussian fitting curve indicates that the maximal probability for crystallite edge length is about 50 nm. Transmission electron microscopy (TEM) micrograph (Figure 2c) clearly shows that those particles are all of octahedral morphology. The corresponding high-resolution transmission electron microscopy (HRTEM) image (Figure 2d) of the selected area marked in Figure 2c shows crystalline character with a lattice spacing of 0.277 nm, which can be indexed to the (200) plane of tetragonal BaMoO₄. The single-crystal structure of the single

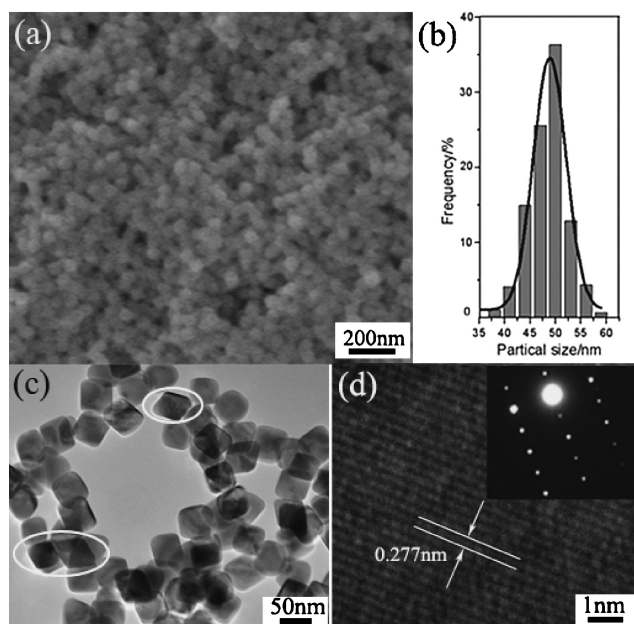


Figure 2. (a) FESEM, (b) the particle size distribution, (c) TEM, and (d) HRTEM and the corresponding SAED of BaMoO₄ prepared at room temperature for 2 days.

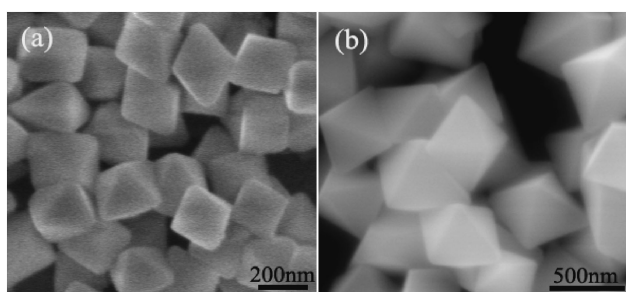


Figure 3. FESEM of BaMoO₄ prepared at different conditions (a) [Ba²⁺] = [MoO₄⁻] = 0.01 M and (b) $\omega = 25$.

octahedron-like barium molybdate nanocrystals is also mirrored in the selected area electron diffraction (SEAD) image shown in the inset of Figure 2d.

A possible growth mechanism for the formation of BaMoO₄ octahedra is reported in the literature.^{7a} The mechanism of the BaMoO₄ nano-octahedra formation in w/o microemulsion in our case is not clear yet, but we believe that the anisotropic growth of BaMoO₄ nano-octahedrons, the reagent concentration, and the molar ratio of water and Triton X-100 play critical roles in the morphology and size control of BaMoO₄ nanocrystals. We can realize the size tuning of these BaMoO₄ nano-octahedral conveniently by changing the above-mentioned parameters. For instance, when the reagent concentration was reduced to 0.01 M or ω was increased to 25 in the microemulsions, the average edge length of the octahedral particles is 300 (Figure 3a) and 600 nm (Figure 3b), respectively. Such prepared nano-octahedral BaMoO₄ may have unique size-dependent photolumines-

cence properties due to quantum effects, and corresponding research is underway.

In conclusion, we have prepared uniform BaMoO₄ nano-octahedra by a facile reverse microemulsion at room temperature. These average particle size of BaMoO₄ nano-octahedras can be modulated by microemulsion method. These nanoscale structures should exhibit excellent properties and be potential building blocks for advanced electronic and optoelectronic devices. This approach can be extended to prepare other related nanoscale inorganic materials.

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