Novel Shape Evolution of BaMoO₄ Microcrystals

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Dendritic BaMoO₄ microcrystals with lengths of about $5-15 \mu m$ were synthesized simply under ambient conditions by a microemulsion-mediated method within an ultrashort time. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and field-emission scanning electron microscopy (FESEM), which showed that the products were in pure tetragonal BaMoO₄ structure and that an individual dendrite had a long central stem with four array shrunken branches. Detailed studies revealed that the formation of these 3-D structures was strongly dependent on the composition of the microemulsion. At prolonged aging time, the dendrites evolved into rods and further into particles, driven by the lattice distortion energy required to evolve the crystal from a metastable to a stable state. This novel crystal shape evolution provides insight into crystallization behavior given that the growth history and shape evolution process have traditionally been poorly understood.

Introduction

The fabrication of nano- to microscale inorganic materials with special size and morphology is of great interest for the study of material chemistry because of the importance in basic scientific research and potential technological applications of such materials.^{1–3} In the past few years, considerable efforts have been focused on the synthesis of inorganic crystals with various morphologies, such as 0-D (particles and polyhedra), 1-D (rods, wires, belts, and tubes), 2-D (disks and plates), and 3-D (multipods, snowflakes, hyperbranches, and dendrites) structures. Of these abundant shapes, 3-D hierarchical dendrites have attracted much attention because of the practical importance related to some fractal growth phenomena. Previous studies on dendritic crystals have mostly been focused on specific materials and crystal shapes, limiting the general understanding of the nanocrystal shape evolution process and the possibility of exploiting their growth mechanisms for other materials and geometries. In most cases, the formation of 3-D hierarchical dendrites resulted from the evolution of 0-D or 1-D primary crystals via an oriented attachment process or a selfassembly process induced by the use of selective surfactants, which lead to the production of anisotropic shapes arising from the blocking or retarding of growth along one or more directions through selective adhesion. $^{4-13}$

BaMoO₄ is one of the most important inorganic materials from among the metal molybdate families, which have high potential applications in various fields, such as photoluminescence and hosts for lanthanide-activated lasers.¹⁴ BaMoO₄ has usually been prepared by conventional methods including repeated ball-milling and solid-state reaction. Recently, nanoor microscale BaMoO₄ crystals have been obtained by methods using a polymerized complex or catanionic reverse micelles.^{15,16} In their synthesis, high temperatures or long reaction times are necessary for the formation of 3-D hierarchical structures. Presently, our group has prepared CaMoO₄ and SrMoO₄ mesocrystals via a microemulsion-mediated route.¹⁷ In this article, we describe the successful preparation of hierarchical dendrites of BaMoO₄ by a similar method at room temperature in an ultrashort reaction time, as well as the observation of shape evolution from dendrites to rods and further to particles with different aging times. To the best of our knowledge, these peculiar shape evolutions of crystals from 3-D to 1-D and 0-D structures have not been reported by previous researchers. Therefore, studies on the shape control and evolution of BaMoO₄ crystals will, to some extent, provide insight into crystallization behavior given that the growth history and shape evolution process have traditionally been poorly understood.

Experimental Section

Analytical-grade Na₂MoO₄•2H₂O, BaCl₂•2H₂O, *n*-octane, *n*-butanol, and cetyltrimethylammonium bromide (CTAB) were purchased from Shanghai Chemical Industrial Company and were used without further purification. The reaction was carried out in a 50-mL glass jar (reaction temperatures lower than 100 °C) or in a 50-mL Teflon-lined stainless steel autoclave (reaction temperatures above 100 °C).

The synthesis of BaMoO₄ microcrystals was achieved simply, via a microemulsion-mediated route. In a typical procedure, two microemulsion solutions were prepared by adding 1.96 mL of 0.2 M BaCl₂ and 1.96 mL of 0.2 M Na₂MoO₄ aqueous solutions to separate *n*-octane/CTAB/*n*-butanol systems (molar ratio of water to surfactant $\omega = 33$, molar ratio of *n*-butanol to CTAB p = 3.60, and [CTAB] = 0.2 M), which were stirred for 30 min until they became transparent. Then, the two solutions were mixed rapidly under vigorous stirring and aged at room temperature (25 °C) for different times (from 1 min to 150 h). The white products were separated by centrifugation, washed with deionized water and absolute ethanol several times, and

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Figure 1. XRD pattern of a sample formed after being aged at room temperature for 1 min ([CTAB] = 0.2 M, ω = 33).

then dried in a vacuum at 60 °C for 6 h. The as-prepared products were characterized by powder X-ray diffraction (XRD, Shimadzu XRD-6000 instrument with Cu K α radiation, $\lambda = 1.5406$ Å), field-emission scanning electron microscopy (FESEM, FEI SIRION 200), transmission electron microscopy (TEM, JEM 100CX), and high-resolution transmission electron microscopy (HRTEM, JEOL 2010).

Results and Discussion

The products with different morphologies obtained in the CTAB/microemulsion system have similar crystalline phases. The XRD pattern (Figure 1) clearly shows that all of the diffraction peaks can be indexed as the pure tetragonal structure with cell parameters a = 5.58 Å and c = 12.82 Å (JCPDS card no. 29-193), which confirms that the as-prepared products are BaMoO₄.

The shape evolutions of the $BaMoO_4$ microcrystals depended on the aging time at room temperature after the two microemulsions were mixed. When the aging time was less than 1 min, tetragonal BaMoO₄ with 3-D microstructures could be easily obtained. The FESEM image in Figure 2a clearly shows that dendritic architectures with lengths of about $5-15 \,\mu m$ along the stem were the exclusive morphology in the product. Further observation revealed that the individual BaMoO₄ dendrites were composed of a long central stem with four shrunken branches. The branches were perpendicular to the stem and were composed of parallel-arrayed particles with lengths of about 50-300 nm, as can be seen. When the aging time was increased to 4 h, the dendrites of BaMoO₄ disappeared and evolved to microrods, which were about $2-10 \ \mu m$ in length and 200-400 nm in diameter. Interestingly, the BaMoO₄ microrods were not straight but rather were similar to bamboo, with concavoconvex surfaces. Furthermore, the microrods were not the exclusive morphology in the products, as a small number of nanoparticles with sizes in the range of 100-300 nm were also found (Figure 2b). If the aging time was increased to 24 h, a large quantity of BaMoO₄ microrods with lengths of less than

was prolonged to 150 h at room temperature. In general, the formation of 3-D architectures of inorganic crystals should require a long growth period. For example, penniform BaWO₄ crystals have been synthesized in catanionic reverse micelles by Qi and co-workers.¹⁸ In their experiments, the *a*-axis-oriented shafts were formed by oriented attachment and fusion of *c*-axis-oriented shuttlelike BaWO₄ nanocrystals along the [100] axis, and then [001]-oriented nanowires or nanobelts grew gradually from the pricks, leading to the formation of a well-defined penniform BaWO₄ nanostructure. This process required a long aging time, and it represents the typical growth process of hierarchical crystals from 0-D to 1-D

 3μ m were observed, and the number of nanoparticles clearly

increased (Figure 2c). Finally, all of the microrods evolved into

nanoparticles that were 100-400 nm in size after the aging time



Figure 2. FESEM images of samples obtained after being aged at room temperature for (a) 1 min, (b) 4 h, (c) 24 h, and (d) 150 h ([CTAB] = 0.2 M, $\omega = 33$).



Figure 3. (a) TEM image of an individual dendritic BaMoO₄ crystal. (b) HRTEM image and (c) ED pattern recorded from the tip of the stem. (d) HRTEM image and (e) ED pattern recorded from tip of the branch. The sample was obtained after being aged at room temperature for 1 min ([CTAB] = 0.2 M, $\omega = 33$).



Figure 4. TEM images of samples obtained after being aged at room temperature for (a) 1 min, (b) 1 h, (c) 4 h, (d) 24 h, and (e) 150 h ([CTAB] = 0.2 M, $\omega = 33$, scale bar = 500 nm).

and then 3-D. However, in our experiments, 3-D dendritic BaMoO₄ crystals were formed within a very short reaction time. To carefully examine the structure of the BaMoO₄ crystals, transmission electron microscopy was used to study the dendrites formed at the early stage. A representative TEM image, shown in Figure 3a, further indicates that the dendrite indeed exhibits a symmetric structure. Figure 3c and e are SAED patterns recorded from the tip of the stem (area 1 in Figure 3a) and the tip of a branch (area 2 in Figure 3a), respectively, of an individual dendrite. (More ED patterns are provided in Figure SI1 of the Supporting Information.) The ED patterns are identical and can be attributed to [010] zone axis diffraction, which suggests that the hierarchical dendrite is a single crystal. Representative HRTEM images of the stem tip (Figure 3b) shows that the lattice fringe has a spacing of 0.320 nm belonging to the (004) lattice plane of the tetragonal BaMoO₄ phase, meaning that the stem grows along the [001] direction. In addition, the typical HRTEM image of the branch tip (Figure 3d) reveals that the lattice spacing of 0.279 nm corresponds to the (200) face, which implies that the protuberant branches are growing along the [100] direction and perpendicular to the [001] direction of the stem. On the basis of the SEM/TEM morphologies and the SAED results, it is reasonable to conclude that the dendritic BaMoO₄ crystals were constructed by a stem along the [001] direction and four branches along the $\langle 100 \rangle$ directions. Careful observation of the HRTEM images of the stem tip and branch tip also clearly indicates the existence of lattice distortion at the specified square area (black arrow in Figure 3b,d). The presence of distortion is generally considered to be the direct

consequence of rapid crystal growth due to the small disorientation of atomic roughness in the interface.¹⁹

To evaluate the evolution process of the BaMoO₄ crystals, TEM images of the samples obtained at different aging times were recorded. The product obtained at a very short aging time (1 min) has a dendritic structure consisting of a long stem with numerous branches on two opposite sides of the stem (Figure 4a). At increasing aging time, the branches grew wider along the stem direction ([001] direction), as shown in Figure 4b. The darker contrast of the branches (Figure 4b) indicates that they are much thicker than those at the initial stage (Figure 4a). It is known that the fast-growing faces of crystal will disappear during crystal growth process. The root area that connects the stem is much thinner than the middle part of the branch, which means that the branches also grow rapidly along the [100] and [010] directions. Unlike in the previous studies of other dendritic materials,^{7–12,16,17} the branches did not grow further along the direction of the stem to form a penniform morphology. In contrast, the branches in the current study grew rapidly along three directions: [001], [100], and [010]. The rapid growth along three directions results in branches resembling spindles. It can also be seen that the regions of the stem between two adjacent branches are much thinner, indicating that the growth of the branches occurred by consuming the stem. An interesting issue regarding the dendrite growth is why the branches grow along three directions. Such an unusual manner of growth of the branches is likely driven by the lattice distortion energy resulting from lattice distortion in the dendritic crystal.^{20,21} The 3-D BaMoO₄ structure was obtained in a very short time, so lattice



Figure 5. (a,b) FESEM images and (c) scheme of particles obtained through the hydrothermal reaction at 160 °C for 24 h ([CTAB] = 0.2 M, $\omega = 33$).

distortions cannot be avoided during the crystallization process. These lattice distortions are confirmed in the HRTEM images of the stem and branch (Figure 3b,d). The dendritic crystals containing numerous lattice distortions are in a metastable structure, so they should evolve to a stable state to minimize the total energy. In this case, highly crystalline particles are more stable than dendritic crystals. Therefore, the branches of the dendritic crystals completely departed from the stem and evolved into nanoparticles when the reaction time was increased to 4 h. That is why a small number of particles coexisted with the rods (Figure 2b). After the branches departed from the stem completely, the stems evolved into zigzag-shaped microrods, as shown in Figure 4c. In accordance with previous studies, we tentatively suggest that the microrods were enclosed by the

slow-growing {011} and {111} faces caused by the disappearance of the fast-growing {100} faces. The microrods further grew along three directions by consuming the thinner area of the stem, and the long rods gradually divided into short rods and particles after being aged for 24 h (Figure 4d). Finally, the rods evolved completely into particles when the aging time was long enough (Figure 4e). The shape of the particles departing from the rods was more like a spindle, indicating that the {001}, {100}, and {010} faces were minimized. Because the departure of the particles from the rods was sequential, the particles experienced different "Ostwald ripening" times, which resulted in their blunt edges and multidispersion in size.

To accelerate the evolution of the BaMoO₄ crystals from dendrites to particles, comparative experiments involving a hydrothermal process were carried out. A similar shape evolution of BaMoO₄ from 3-D to 1-D and 0-D structures was observed within a shorter reaction time (as shown in Figure SI2). Interestingly, when the reaction was performed at 160 °C for 24 h, polyhedral particles with a size of about $0.5-1 \,\mu m$ were the exclusive products (Figure 5a). It is interesting to find that the particles are 18-facet polyhedra, which is very similar to the results obtained in a previous study on PbWO₄.²⁰ On the basis of the above analysis, we can infer that the exposed facets of the polyhedron are two $\{001\}$ faces, eight $\{101\}$ faces, and eight {111} faces, as shown in Figure 5b,c. Unfortunately, we cannot determine this directly from the experimental results obtained by HRTEM or SAED. Judging from the differences between particles obtained at different temperatures, we believe that the high temperature and pressure encountered under hydrothermal conditions accelerate dissolution/recrystallization during the Ostwald ripening process, which results in the increase in size and shearing on the edge.²²

In our study, in addition to the shape evolution of BaMoO₄ crystals from 3-D to 0-D, another interesting issue is how the dendritic crystals develop within a very short time. Detailed experiments revealed that the composition of microemulsion, especially the value of ω (molar ratio of H₂O to CTAB), played a key role in controlling the initial shape of BaMoO₄ in a very short time. Figure 6 shows the TEM image of the as-synthesized products obtained at a CTAB concentration of 0.2 M and an aging time of within 1 min, but with $\omega = 5$, 15, and 30, respectively. For $\omega = 5$, nanoparticles with sizes of 50–100 nm were observed in the products (Figure 6a). For $\omega = 15$, microrods with lengths of 1–3 μ m and widths of 50–80 nm were obtained (Figure 6b). However, when the value of ω was increased to 30, dendritic crystals with lengths of about 3–10



Figure 6. TEM images of samples obtained after being aged at room temperature for 1 min for $\omega = (a) 5$, (b) 15, and (c) 30 ([CTAB] = 0.2 M).



Figure 7. Scheme of BaMoO₄ crystals prepared at different values of ω within a short reaction time.

 μ m were the exclusive products (Figure 6c). The TEM images reveal that the morphologies of the as-synthesized products changed gradually from nanoparticles to microrods and finally to microdendrites with increasing ω value. It was found that the sizes of the crystals obtained by this microemulsion process were many times larger than the typical dimensions of individual microemulsion droplets (5-100 nm) under appropriate reaction conditions.²³ Thus, it can be inferred that the molar ratio of H₂O to CTAB (or the water content) and the aggregation coalescence of individual droplets are both responsible for the formation of products with various morphologies. A schematic diagram of the proposed growth mechanism is shown in Figure 7. When two microemulsion solutions containing Ba^{2+} and MoO₄²⁻ are mixed, nucleation and micelle fusion can occur simultaneously, where BaMoO₄ nucleation is well-known to be very fast. When the ω value is low, the low water content containing few exchangeable water molecules in the microemulsions might cause the fusion rates between two spherical droplets to be very low, which would result in a spherical droplet as shown in Figure 7. Such a microemulsion droplet comprises a centrally located spherical BaMoO₄ nucleus. The subsequent growth occurred at every direction of the spheroid, resulting in the formation of BaMoO₄ nanoparticles. When a moderate ω value is used, the greater amount of exchangeable water in the droplets accelerates the fusion between pairs of droplets. Such fused microemulsion droplets comprise centrally located rodlike BaMoO₄ nuclei with water-enriched domains at the ends of the droplets. The surfactant molecules at the sides of a cylindrical droplet can adsorb onto the surface planes of the formed BaMoO₄ nucleus, so that these surfactant molecules become fixed and immobile. In contrast, the surfactant molecules at the two ends of the cylindrical droplet do not associate with the BaMoO₄ nucleus because of water-enriched domains in these regions and are relatively free. Thus, a cylindrical microemulsion droplet can dynamically and rapidly interact with other microemulsion droplets at both ends of the droplet.^{24,25} This process can result in the formation of 1-D BaMoO₄ microrods along the fast-growing [001] direction. When the ω value is high, the formed droplets system might significantly increase the fusion rate. With the water-enriched domains, the surfactant molecules at the sides of the cylindrical droplet cannot stably adsorb on the surfaces of the formed BaMoO₄ nucleus and limit the growth direction of the nucleus. Thus, the nucleus can also grow along the [100] and [010] directions, which are perpendicular to the fast-growing [001] direction. This process can result in the formation of 3-D dendritic BaMoO₄ crystals. From the model and the experiment results, we can conclude that the initial shape

of the BaMoO₄ crystals is strongly dependent on the ω value of the microemulsion.

Conclusions

In summary, we report a novel shape evolution of BaMoO₄ crystals from 3-D dendrites to 1-D rods and to 0-D particles with prolonged aging time. Minimization of the lattice distortion energy is assumed to drive the metastable dendrites to divide into stable particles. In contrast to the traditional crystal growth from 0-D to 1-D to 3-D, in this case, 3-D dendrites were easily obtained within a very short reaction time. Detailed experimental results revealed that the composition of the microemulsion, especially the ω value, controls the initial shape of the BaMoO₄ particles. This method can be extended to other materials to purposefully prepare 0-D, 1-D, and 3-D structures. In fact, we have observed a similar shape evolution process in BaWO₄.

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Supporting Information Available: ED patterns recorded from a single dendritic BaMoO₄ crystal and TEM images of samples obtained by a hydrothermal reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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