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Morphological Evolution of $SrMoO_4$ Crystals from Wires to Notched Spheres through Oriented Attachment

Eun-Jee Choi and Young-Duk Huh*

*Department of Chemistry, Dankook University, Gyeonggi-Do 448-701, Korea. *E-mail: ydhuh@dankook.ac.kr*
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The fabrication of hierarchical inorganic microstructures has attracted great interest because of their unique, shape-dependent properties and applications.[1-5] In general, hierarchical microstructures have been synthesized by using template precursors such as surfactant micelles, copolymer aggregates, and microemulsion droplets.[6-9] $SrMoO_4$ is an important optical material that is widely used in Raman converters and solid-state lasers.[10,11] However, only a few groups have examined synthetic methods for the fabrication of assembled $SrMoO_4$ structures. $SrMoO_4$ nanorods were synthesized *via* a hydrothermal reaction.[12] Various shapes of $SrMoO_4$ were prepared by a simple alkaline aqueous mineralization method.[13] Hierarchical, three-dimensional structures of $SrMoO_4$ have been prepared with microemulsion methods.[6,14] In this paper, we report the morphological evolution of $SrMoO_4$ crystals obtained using reverse microemulsion with sodium bis(2-ethylhexyl) sulfosuccinate (NaAOT) surfactant. The morphological evolution of the $SrMoO_4$ crystals obtained by a simple precipitation method without any surfactants or templates was also examined.

Experimental Section

$Sr(NO_3)_2$ (Aldrich), $Na_2MoO_4{\cdot}2H_2O$ (Aldrich), isooctane (Aldrich), and NaAOT (TCI) were used as-received. For the typical synthesis of self-assembled $SrMoO_4$ crystals using a simple precipitation method, 10 mL of 0.1 M $Sr(NO_3)_2$ aqueous solution was added to 10 mL of 0.1 M $Na_2MoO_4{\cdot}2H_2O$ aqueous solution under stirring for 1 min, after which the reaction mixture was incubated for 24 h at room temperature. To investigate the effects of concentrations of $Sr(NO_3)_2$ and $Na_2MoO_4{\cdot}2H_2O$, different concentrations (0.1 M, 0.2 M, 0.3 M, and 0.4 M) were used.

Synthesis of $SrMoO_4$ in AOT water-in-oil microemulsions was undertaken as follows. First, $Sr(AOT)_2$ was prepared by mixing 1 L of 22.5 mM NaAOT aqueous solution with 1 L of 27.0 mM $Sr(NO_3)_2$ aqueous solution at room temperature. The resulting white precipitate of $Sr(AOT)_2$ was centrifuged, washed with water and then dried under vacuum. $Sr(AOT)_2$ was then dissolved in isooctane at a weight ratio of 1:6. The final product of $Sr(AOT)_2$ was obtained by using a rotary evaporator. Typically, 1.8 mL of 50 mM Na_2MoO_4 aqueous solution was added with shaking to 100 mL of a 200 mM NaAOT solution dissolved in isooctane to give a suspension of microemulsion droplets with a water to surfactant molar ratio, i.e., $[H_2O]/[NaAOT]$, of $w = 5$. To introduce Sr^{2+} ions into the reaction, 4.0 mL of 50 mM Sr $(AOT)_2$ reverse micelles dissolved in isooctane was added to 100 mL of the molybdate-containing microemulsion. To investigate the effect of the AOT concentration and isooctane amount, various concentrations of NaAOT and amounts of isooctane were used with other conditions fixed. The mixture was then incubated for 24 h at room temperature.

The structures of the as-prepared $SrMoO_4$ products were analyzed by powder X-ray diffraction (XRD, PANalytical, X'pert-pro MPD) with Cu-Kα radiation. The morphologies of the products were characterized using scanning electron microscopy (SEM, Hitachi S-4300) and transmission electron microscopy (TEM, JEOL JEM-3010). The Raman spectra of the products were obtained with a Raman spectrometer (HORIBA Jobin Yvon T64000) with a radiation of 514.5 nm from an argon ion laser.

Results and Discussion

Figure 1 shows the XRD patterns and Miller indices of the $SrMoO_4$ crystals obtained using a simple precipitation method. All peaks corresponded to tetragonal $SrMoO_4$ and matched the reported data for this system (JCPDS 08-0482, $a = 5.394$ Å, and $c = 12.02$ Å). The Raman spectrum of these $SrMoO_4$ crystals is shown in Figure 2. The Raman peak at 880.0 cm^{-1} was assigned to the symmetric stretching vibration mode v_1 (A_g) of the MoO_4^{2-} group in the $SrMoO_4$ crystal. The peaks at 847.5 and 799.6 cm^{-1} corresponded to the anti-symmetric stretching v_3 (B_g) and v_3

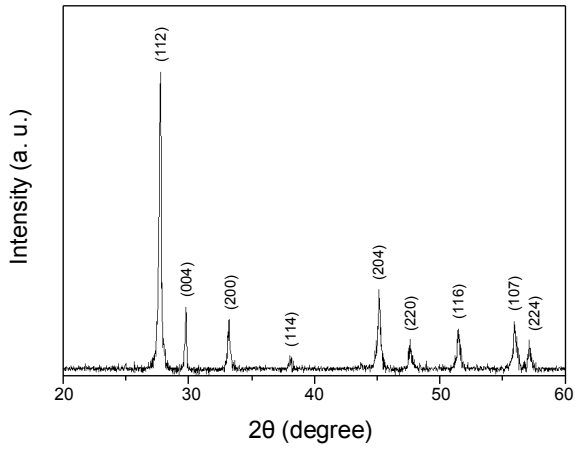


Figure 1. XRD patterns and Miller indices of the $SrMoO_4$ crystals obtained from the precipitation reaction.

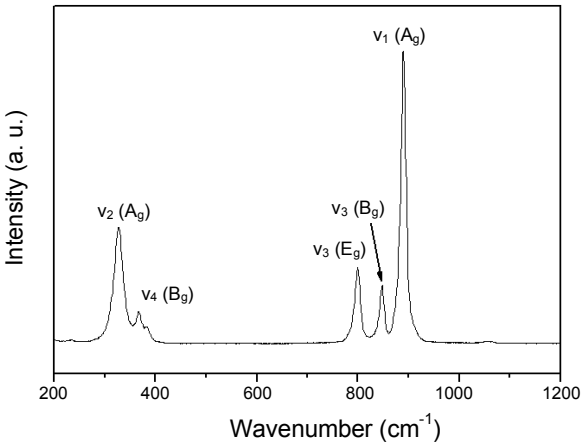


Figure 2. Raman spectra of the $SrMoO_4$ crystals obtained from the precipitation reaction.

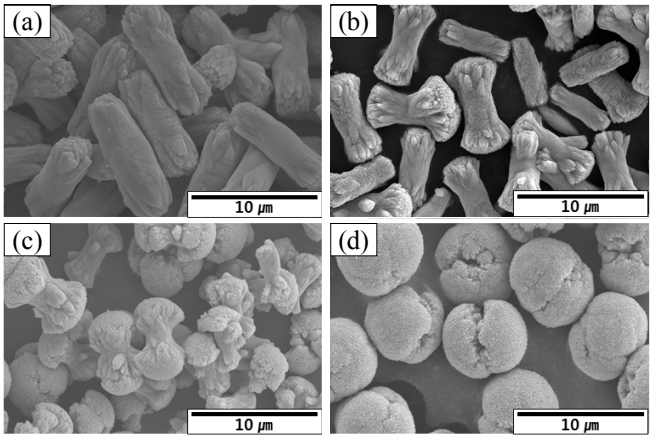


Figure 3. SEM images of the $SrMoO_4$ crystals obtained at various concentrations of $[Sr(NO_3)_2] = [Na_2MoO_4]$ by the precipitation reaction: (a) 0.1 M, (b) 0.2 M, (c) 0.3 M, (d) 0.4 M.

(E_g) vibration modes, respectively. The peaks at 368.0 and 328.4 cm^{-1} corresponded to the anti-symmetric and symmetric v_4 (B_g) and v_2 (A_g) bending modes, respectively.[15,16] No other peaks were detected in the XRD and Raman spectra, we concluded that $SrMoO_4$ was successfully synthesized.

Figure 3 shows SEM images of the $SrMoO_4$ products obtained by the precipitation method using various concentrations of Sr^{2+} and MoO_4^{2-} ions. At $Sr(NO_3)_2$ and Na_2MoO_4 concentrations of 0.1 M, rod-like $SrMoO_4$ crystals of average length 10 μm were formed (Figure 3a). At $Sr(NO_3)_2$ and Na_2MoO_4 concentrations of 0.2 M, the morphology of the crystals resembled peanuts with round faces at the ends of the crystals, which were starting to branch (Figure 3b). With increasing $Sr(NO_3)_2$ and Na_2MoO_4 concentrations, the morphology of the $SrMoO_4$ crystals changed to notched spheres *via* dumbbells (Figures 3c and 3d). As the $SrMoO_4$ crystals were obtained by the simple precipitation method without any surfactants or templates, their morphologies, such as rods, peanuts, dumbbells, and notched spheres, were attributed to the natural properties of the $SrMoO_4$ crystal structures.

To investigate the morphology of the small $SrMoO_4$ crystals,

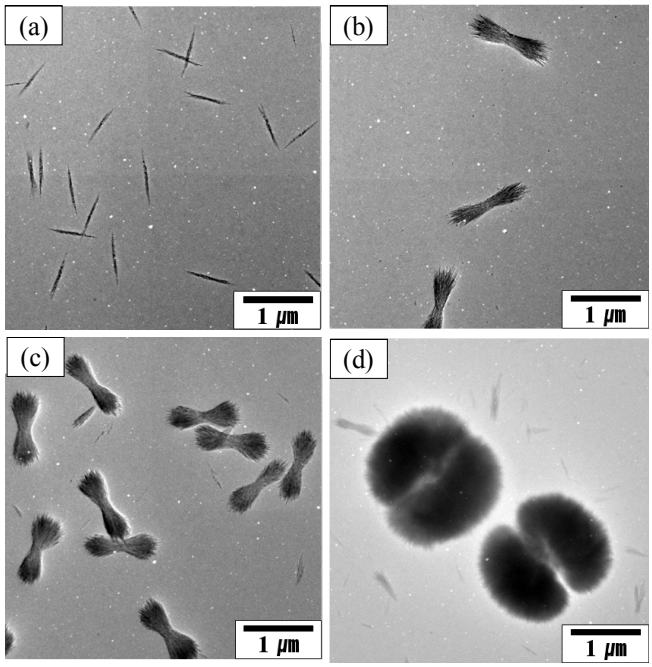


Figure 4. TEM images of the $SrMoO_4$ crystals obtained at various concentrations of NaAOT with $[Sr(NO_3)_2] = [Na_2MoO_4] = 0.05$ M by the microemulsion method: (a) 0.05 M, (b) 0.067 M, (c) 0.1 M, (d) 0.2 M.

we used the reverse microemulsion method with NaAOT as an anionic surfactant. Figure 4 shows TEM images of the $SrMoO_4$ crystals obtained with various concentrations of the anionic surfactant. At [NaAOT] = 0.05 M, $SrMoO_4$ wires of average length 0.7 μm were formed, as shown in Figure 4a. At [NaAOT] = 0.067 M, the $SrMoO_4$ crystals resembled haystacks. The wires were assembled in a side-by-side geometry. The waist width of the haystack-like, $SrMoO_4$ crystals was approximately 150 nm. The morphology of the $SrMoO_4$ crystals evolved from wires to notched spheres as the wires were assembled in a side-by-side geometry. With few $SrMoO_4$ wires, they preferred to lie parallel to each other with a strong attachment at the middle of the haystacks. More numerous $SrMoO_4$ wires were formed with increasing AOT concentration in the droplet of the microemulsion method. With increasing number of $SrMoO_4$ wires, the assembly forces of the wires decreased at both ends of the crystals and the $SrMoO_4$ products formed as spheres to minimize the chemical potentials of the self-assembled structure of the $SrMoO_4$ crystals. As the middle of the $SrMoO_4$ crystals continued to be strongly self-assembled by the side-by side alignment, the final $SrMoO_4$ products assumed a notched sphere shape, as shown in Figure 4d. Therefore, the morphology of the $SrMoO_4$ crystals evolved to a final shape of notched spheres with increasing AOT concentration. A similar result was obtained by changing the amount of isooctane in the microemulsion system. The morphology of the $SrMoO_4$ crystals changed from haystacks, through peanut-like, to notched spheres with decreasing isooctane amount, as shown in Figure 5.

Figure 6(a) shows high-resolution TEM (HRTEM) images of individual $SrMoO_4$ wire obtained with [NaAOT] = 0.05 M by the microemulsion method. Figure 6(b) shows the tip area of an individual wire. The width of the individual wire was approxi-

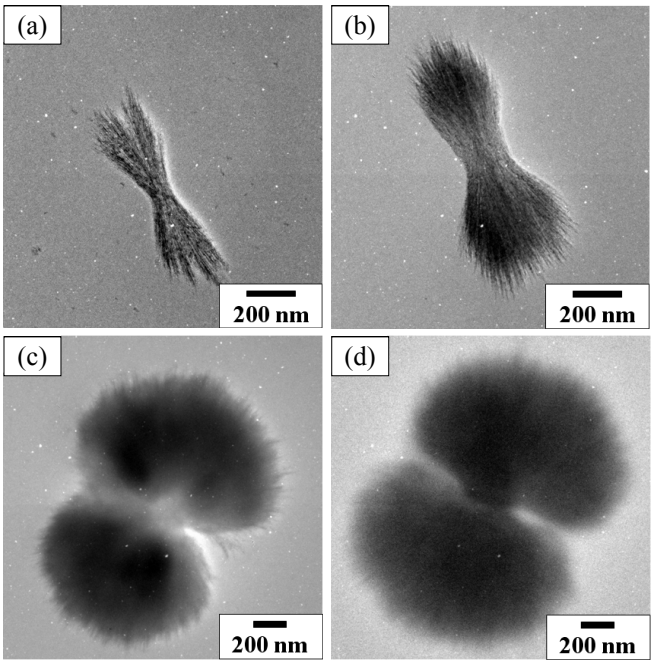


Figure 5. TEM images of the $SrMoO_4$ crystals obtained at various amounts of isooctane with $[Sr(NO_3)_2] = [Na_2MoO_4] = 0.05$ M by the microemulsion method: (a) 400 mL, (b) 300 mL, (c) 200 mL, (d) 100 mL.

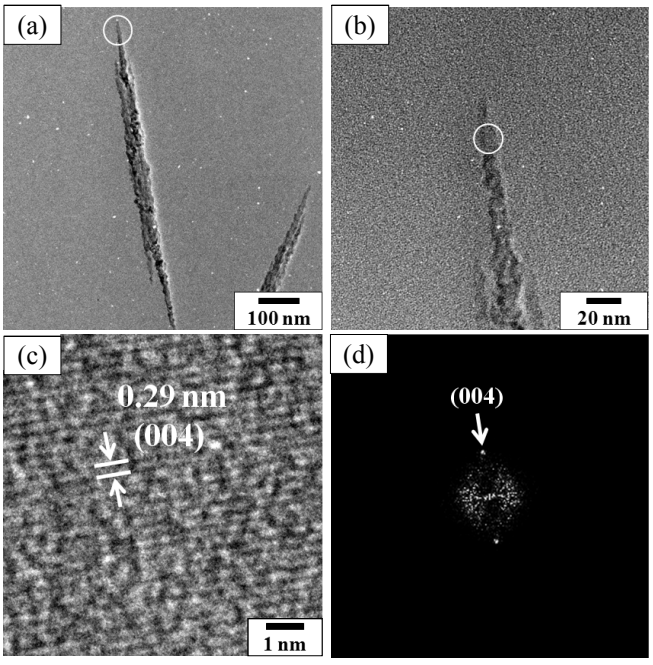


Figure 6. (a) and (b) HRTEM images, (c) fringe patterns, (d) FFT patterns of the $SrMoO_4$ crystals obtained with [NaAOT] = $[Sr(NO_3)_2] = [Na_2MoO_4] = 0.05$ M by the microemulsion method.

mately 10 nm. The observed lattice spacing of 0.29 nm corresponded to the (004) plane of tetragonal $SrMoO_4$ crystals, as shown in Figure 6(c). Figure 6(d) shows the fast Fourier transform (FFT) patterns corresponding to the lattice fringes.

Individual wires of the $SrMoO_4$ crystals exhibited a growth preference along the <001> direction, as shown in Figure 6. This indicated that the axes of the wires of the $SrMoO_4$ crystals were aligned along the crystallographic *c*-axis. $SrMoO_4$ crystals with haystack-like shapes were formed by assembling the wires in a side-by-side geometry with oriented attachment. With increasing number of $SrMoO_4$ wires, the oriented attachment of each wire was weakened at both ends of the $SrMoO_4$ products. The $SrMoO_4$ crystals changed from wire to notched spheres *via* an intermediate stage of haystack and peanut morphology. Therefore, the $SrMoO_4$ crystals exhibited a unique growth pattern in which the wires were self-assembled in a side-by-side geometry with oriented attachment for the formation of the final notched spheres of $SrMoO_4$ crystals.

Conclusion

Well-crystallized $SrMoO_4$ products with various shapes were synthesized by a simple method of precipitation and microemulsion using an anionic surfactant AOT microemulsion. The resulting $SrMoO_4$ crystals exhibited wire-, haystack-, peanut-, dumbbell-, and notched sphere-like shapes. With increasing AOT concentration, the morphology of the $SrMoO_4$ crystals evolved from wires, through haystacks and dumbbells, to notched spheres with higher hierarchy, and from rod- and peanut-like shapes to notched spheres with increasing Sr^{2+} and MoO_4^{2-} ion concentrations, in a simple precipitation reaction. This morphological evolution of the $SrMoO_4$ crystals was attributed to an oriented attachment.

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