

Shape and size control of inorganic nanoparticles using microemulsion method

Toshiyuki Nomura, Hiroaki Arima, Toshihiro Mori and Yasuhiro Konishi

Chemical Engineering Department, Osaka Prefecture University,
1-1, Gakuen-cho, Sakai, Osaka 599-8531, Japan
Fax: 81-72-254-9911, e-mail: nomura@chemeng.osakafu-u.ac.jp

Inorganic nanoparticles have electrical and optical properties that depend sensitively on shape and size. If the shape and size of the nanoparticles can be controlled, it can be expected as a new material which brings about new technological innovation. In this study, it is reported that the shape and size of the nanoparticle can be controlled by utilizing the water-in-oil microemulsion as nanometer-sized reaction medium. Barium chromate as model particles was synthesized using the water-in-oil microemulsion formed by AOT as anionic surfactant, and isooctane as organic solvent. Bundles of nanowires, chains of nanorods, and superlattice structure of nanodots were synthesized by changing raw material concentration, raw material molar ratio, and reaction temperature. Crystal growth can be suppressed by a surfactant selectively absorbed onto the crystal faces of barium chromate. In addition, the higher order structures are formed by self-organization of the nanoparticles by hydrophobic interactions between the surfactant molecules absorbed onto the nanoparticles. Finally, it is demonstrated that the shape and size of the nanoparticles can be controlled by the particle-surfactant interaction and the number of the generated particles wherein the latter depends on the supersaturation ratio and the reaction temperature.

Key words: Nanorod, Nanowire, Microemulsion, Self-organization, Particle-surfactant interaction

1. INTRODUCTION

Recently, the synthesis of inorganic nanoparticles has been achieved by various methods. However, it is difficult to synthesize nanorods and nanowires by controlling the shape and size of the nanoparticles. Such nanoparticles exhibit electrical and optical properties that depend sensitively on shape and size^[1-2]. Therefore, new technological innovations require the control of shape and size of the nanoparticles. There have been proposed several methods for shape and size control of inorganic nanoparticles in liquid phase: template synthesis method using the surfactant as a mold^[3], growth suppression method of specific crystal face by injection of precursor molecules into a hot surfactant^[4-6], solvothermal method under high temperature and pressure^[7-9], and microemulsion method using interfacial activity of reverse micelles and microemulsions^[10-12]. However, it does not mean that the morphology of the product material can be freely controlled by these methods. Furthermore, the nature of the possible synthetic chemical compound is also limited.

This paper describes the shape and size control of barium chromate nanoparticles by the microemulsion method. The effects of aqueous composition and temperature on the particle morphology are examined both experimentally and theoretically.

2. EXPERIMENTAL

Two kinds of water-in-oil microemulsion solutions were prepared by adding 0.18ml of aqueous Ba(NO₃)₂ or Na₂CrO₄ (40-320mol/m³) to 10ml of solutions of NaAOT (dioctyl sodium sulfosuccinate, C₂₀H₃₇NaO₇S) dissolved in isooctane (100mol/m³). The surfactant mole ratio was $w = [\text{H}_2\text{O}]/[\text{NaAOT}] = 10$. Ba²⁺-containing

microemulsion 5ml was mixed with CrO₄²⁻-containing microemulsion 5ml using the vortex mixer. The mixed solution was stood in one week, while it was kept at constant temperature (298, 333K). The morphology of the product material was observed using transmission electron microscope TEM (JEOL, JEM-2000FX) and scanning electron microscope SEM (Hitachi, S-4500). Samples were prepared by putting the solution containing the product material on TEM grids and SEM stage, and air-dried, washed with pure isooctane and dried under vacuum. The product materials were characterized by selected area electron diffraction (SAED) and energy dispersive X-ray analysis (EDXA). All materials were of analytical grade (purity > 98%), used without further purification as purchased from Nacalai tesque.

3. RESULTS AND DISCUSSION

Figure 1 shows TEM and SEM photographs of the product material resulting from equal initial concentrations of barium ion and chromate ion of 40mol/m³. The corresponding results of EDXA are shown in Table I. In this study, this condition was made to be the standard condition. The product material was the bundle in which the nanowire was self-organized, and the space of the generated particle was about 2nm. Electron diffraction (SAED) showed that the nanowire elongated along the *a* axis. Elemental analysis (EDXA) showed that the product material contained BaCrO₄ and the surfactant AOT, which constitute elements of Ba, Cr, O, C and S having these composition ratios. These results indicate that the AOT molecule has selectively adsorbed on the faces along the *a* axis. The formation of bundle on nanowires is considered as following:

1. The AOT molecules chemically adsorb on specific crystal faces of the generated particle by strong interactions such as electrostatic attraction, and charge-transfer.
2. The nanowire is formed by suppressing the growth of the adsorption faces of the AOT molecules.
3. Nanowires are self-organized by the hydrophobic interaction of hydrophobic group of the AOT molecule adsorbed onto particle.

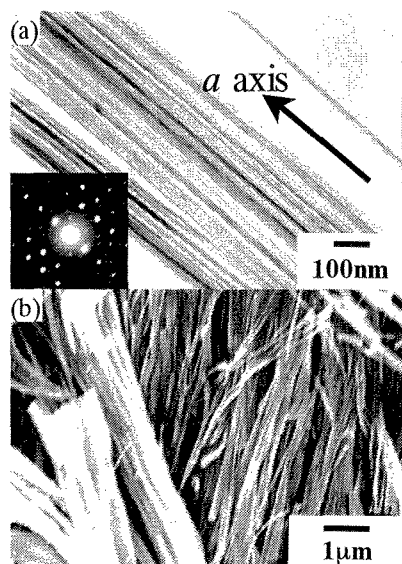


Fig.1 BaCrO₄ nanostructure under standard condition ([Ba²⁺] = [CrO₄²⁻] = 40mol/m³, 298K), (a) TEM photograph. Inset, electron diffraction pattern from an individual fiber, (b) SEM photograph.

Table I Energy dispersive X-ray analysis of product material under standard condition ([Ba²⁺] = [CrO₄²⁻] = 40mol/m³, 298K).

	wt%	atomic%
Ba	35.1	5.8
Cr	11.3	5.0
O	19.2	27.5
C	30.9	59.2
S	3.5	2.5

Figure 2 shows the TEM photographs of the product material at different concentration of chromate ion. The morphology of the product material changed to bundle of nanowires (Fig.1), chain of nanorods (Fig.2(a)), and superlattice structure of nanodots (Fig.2(b)). The aspect ratio of the generated particle decreased with increase in the chromate ion concentration.

The observed effect of chromate ion concentration on the product morphology can be simply explained as follows. The length L of a particle for a axis can be expressed as

$$L = V/NA, \quad (1)$$

where V is the total volume of the generated particles, N

the number of the generated particles, and A (100) face area of a particle. A schematic drawing of the BaCrO₄ nanoparticle is shown in Figure 3. Under this experimental condition, the total volume V was constant based on the stoichiometry, because the concentration of barium ion was kept constant at 40mol/m³. As the growth of the crystal face absorbed the surfactant AOT is suppressed, (100) face area A is almost constant. The particle number N exponentially increases as a function of supersaturation ratio S defined in the following equation

$$S = ([Ba^{2+}][CrO_4^{2-}]/K_{sp})^{1/2}, \quad (2)$$

where K_{sp} is the solubility product of BaCrO₄. Therefore, the particle number N exponentially increases with increase in the chromate ion concentration. The generated monomer will be mainly consumed further than the anisotropic growth for the particle generation with increase in the chromate ion concentration. It is possible to qualitatively explain the tendency of the experimental results.

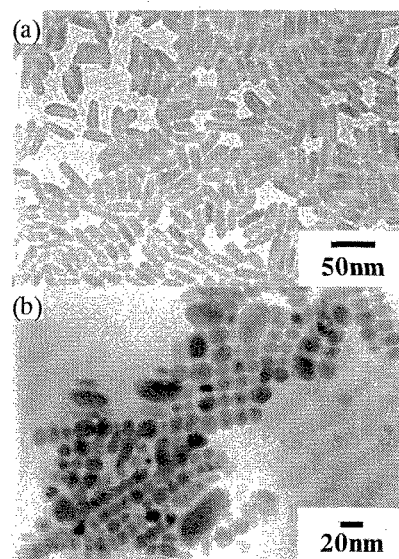


Fig.2 Effect of chromate ion concentration on product morphology ([Ba²⁺] = 40mol/m³, 298K), (a) [CrO₄²⁻] = 80mol/m³, (b) [CrO₄²⁻] = 160mol/m³.

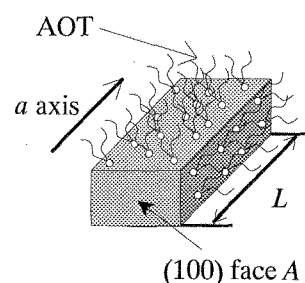


Fig.3 Schematic drawing of BaCrO₄ nanoparticle (V ; total volume of generated particles, A ; (100) face area of a particle, N ; number of generated particles, L ; length of a particle for a axis ($=V/AN$)).

Figure 4 shows the TEM photographs of the product

material at different concentration of barium ion. The morphology of the product material was a bundle of nanowires, regardless of the barium ion concentration.

It is possible to explain why the aspect ratio of the product material did not change with the barium ion concentration: NaAOT precipitates as $\text{Ba}(\text{AOT})_2$ when barium ions are added to the NaAOT aqueous solution. The product of free barium ion concentration and AOT ion concentration which exist in the system is constant, because $\text{Ba}(\text{AOT})_2$ has a poor solubility in water ($[\text{Ba}^{2+}][\text{AOT}]^2 = \text{constant}$). The micelles are formed when the AOT concentration is over the critical micelle concentration (CMC). The AOT ion is consumed by reaction with the barium ion, the AOT ion is supplied from the micelles, therefore the AOT ion concentration always remains saturated. Thus, it is interesting know that the free barium ion concentration also becomes consequently constant. Then the supersaturation ratio S is also constant regardless of the barium ion concentration. As a result, the number N of the generated particles is also constant. Under this experimental condition, as well as the above mentioned, the total volume V and (100) face area A are almost constant. From the above description, it follows that the aspect ratio of product material does not change, even if the barium ion concentration changes. This fact agrees qualitatively well with the tendency of the experimental results.

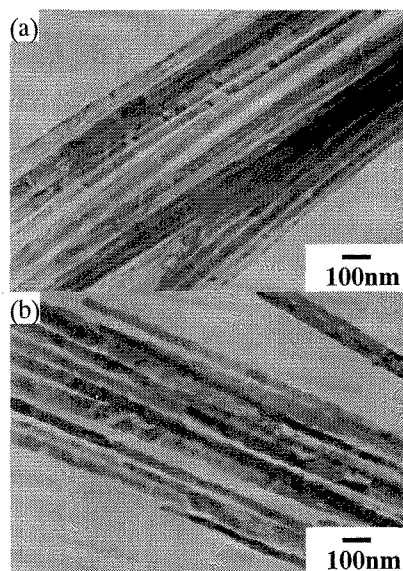


Fig.4 Effect of barium ion concentration on product morphology ($[\text{CrO}_4^{2-}] = 40 \text{ mol/m}^3, 298\text{K}$), (a) $[\text{Ba}^{2+}] = 80 \text{ mol/m}^3$, (b) $[\text{Ba}^{2+}] = 160 \text{ mol/m}^3$.

From the above consideration, chromate ion seems to be the excess in the reaction field, because free barium ion concentration is thin. This fact means that the generated particles have been charged negatively. The electrostatic repulsive force will work between particles-surfactant, because AOT is anionic surfactant. However, the AOT molecule has selectively adsorbed onto the particle. It is guessed that the sulfone group of the AOT molecule works as a ligand, and the barium is selectively recognized. As a result, adsorption charge-transfer complex has been formed on the particle.

Figure 5 shows the effect of raw ion concentration on the product morphology at molar equivalence ($[\text{Ba}^{2+}] = [\text{CrO}_4^{2-}]$). With the increase in the raw ion concentration, the structure of the product material changed to bundle of nanowires (Fig.1), chain of nanorods (Fig.5(a)), and superlattice structure of nanodots (Fig.5(b), (c)). It was proven that the aspect ratio of the generated particles decreased with increase in the raw ion concentration. The reason follows the same argument presented above. Figure 6 shows a schematic diagram of the relationship among the total volume V , (100) face area A , the particle number N and the chromate ion concentration. It is possible to consider the (100) face area A being almost constant, because the surfactant adsorbed onto the particle surface in all experimental conditions. From the stoichiometry, the total volume V increases in proportion to the raw material ion concentration. The particle number N increases exponentially, because the chromate ion concentration increases. It is possible to qualitatively explain the tendency in the experimental result as well as the above.

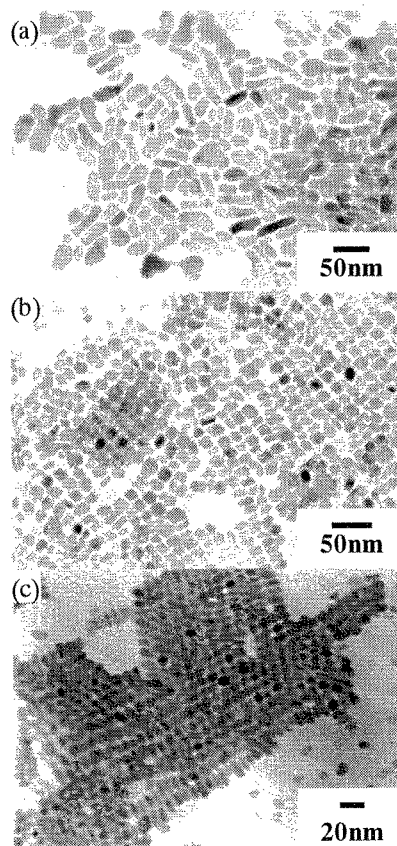


Fig.5 Effect of raw ion concentration on product morphology at molar equivalence ($[\text{Ba}^{2+}] = [\text{CrO}_4^{2-}]$, 298K), (a) 80 mol/m^3 , (b) 160 mol/m^3 , (c) 320 mol/m^3 .

Figure 7 shows the TEM photographs of the product material when the reaction temperature was changed to 333K from the standard condition. The aspect ratio of the generated particle dramatically decreased, when the reaction temperature was increased. This is because the number of the generated particles increased with increase in the reaction temperature.

4. CONCLUSION

The shape and size control of barium chromate nanoparticles by the microemulsion method was examined. It has been shown that the aspect ratio of the generated particles decreased with increase in the chromate ion concentration or the reaction temperature. In contrast, the aspect ratio did not change, even if the barium ion concentration changed. The surfactant AOT has selectively adsorbed on the specific crystal face along the a axis. And, the generated particles were self-organized by the hydrophobic interaction of hydrophobic group of the AOT molecule adsorbed onto particle. The morphology of the nanoparticle depends on the particle-surfactant interaction and the number of the generated particles wherein the latter depends on the supersaturation ratio and the reaction temperature.

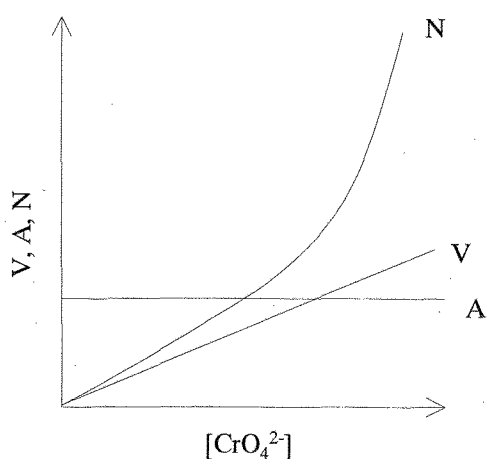


Fig.6 Schematic diagram of relationship among total volume V of generated particles, (100) face area A of a particle, number N of generated particles and chromate ion concentration.

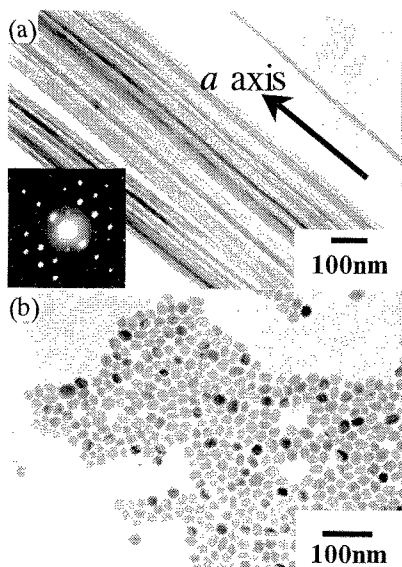


Fig.7 Effect of reaction temperature on product morphology ($[Ba^{2+}] = [CrO_4^{2-}] = 40 \text{ mol/m}^3$), (a) 298K (standard condition), (b) 333K.

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