

Rod-shaped Hydroxyapatite Nanoparticle Formation Using AOT and Water without Oil

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We synthesized rod-shaped hydroxyapatite (HAP) nanoparticles using sodium bis(2-ethylhexyl) sulfosuccinate (AOT) as an additive in water without an oil. The length of the particles increases from 40 to 100 nm with increasing the concentration ratio AOT/Ca while maintaining a width of 12 nm. These results indicate that an oil phase is not necessarily needed to form the rod-shaped HAP nanoparticles using AOT.

The surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) is widely used to prepare nanosized W/O microemulsions.¹ The AOT-based W/O microemulsions have been used for nanoparticle formation.²⁻⁵ When two kinds of W/O microemulsions containing reactants in the water phase are mixed together, the nanoparticles are formed as the nanosized W/O microemulsions act as templates. In some cases,⁶⁻⁸ rod-shaped nanoparticles larger than the W/O microemulsions are formed. It is unclear if the rod-shaped particle formation is attributed to the template effect or not. Li and Mann reported that rod-shaped BaSO₄ particles are formed using W/O microemulsions.⁶ They proposed a mechanism that W/O microemulsions connect together in a straight line and that the particles are formed along the line. However, it is difficult to believe the mechanism because the water droplets move so fast in an oil phase that such a straight-lined connection is difficult to form.

It was also reported that rod-shaped hydroxyapatite (HAP) nanoparticles are formed using the AOT-base W/O microemulsions.^{7,8} HAP has been used as artificial bone materials^{9,10} and chromatomediums.^{11,12} Preparation of HAP particles having various morphologies is an important task to enhance the potential of HAP particles for other applied uses. For example, rod-shaped HAP particles have been studied as a composite material for polymers to control mechanical properties.^{13,14} Sarda et al. suggested that rod-shaped HAP nanoparticle formation using AOT-base W/O microemulsions is induced by an interaction between calcium ions and sulfonate head-groups of AOT at the W/O interface.⁷ It is understandable that the interaction is a key role for the formation. However, we have a question; is the oil phase needed for the formation with AOT? The necessity of an oil phase for the rod-shaped HAP nanoparticle formation has not been investigated so far. Particle formation using W/O microemulsions has a disadvantage in that the productivity is much lower than particle formation using only aqueous solutions, because phase separation occurs if the amount of water and/or salt concentration in the water phase is increased. Therefore, rod-shaped particle formation without an oil phase is important in light of engineering. In this study, we

investigated the formation using an aqueous AOT solution by changing the molar ratio of AOT and calcium ion.

Reagents used were Ca(NO₃)₂ (≥99.5%), (NH₄)₂HPO₄ (≥99.0%), 10% aqueous NH₃ solution from Wako Pure Chemicals, and AOT (98%) from Aldrich. All reagents were used as received. Pure water of 18.2 MΩ cm was prepared using a Direct-Q System (Nihon Millipore). 0.5 M solutions of Ca(NO₃)₂ and (NH₄)₂HPO₄, 1 M solution of NH₃, and 0.02 M solution of AOT were prepared with pure water. 5 mL of Ca(NO₃)₂ solution and 12.5 mL of a mixture of the AOT solution and pure water were poured into a 50-mL glass tube to mix them, where the ratio AOT/Ca was adjusted from 0 to 0.1 by changing the volume of the AOT solution and pure water. The solution pH was adjusted to 10 by adding an NH₃ solution. 3 mL of (NH₄)₂HPO₄ solution was poured into a 10-mL glass tube, and the solution pH was adjusted to 10 by adding an NH₃ solution. After heating these solutions at 40 °C separately, the (NH₄)₂HPO₄ solution was gently poured into the Ca(NO₃)₂ solution with or without AOT with shaking. Finally, the Ca/P ratio was 1.67. The mixture in the capped tube was stored at 40 °C for 24 h. Then it was centrifuged for 30 min at 3500 rpm, and the residual particles were twice washed in acetone and pure water to remove AOT and unreacted ions followed by drying them under vacuum over night.

To characterize the synthesized particles, X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT 2500 diffractometer with Cu Kα radiation at an X-ray tube voltage of 40 kV and a current of 200 mA. Images by scanning transmission electron microscopy (STEM) were recorded on a Hitachi S4300 field emission scanning electron microscope equipped with a transmission electron detector operated at an acceleration voltage of 30 kV. Samples were prepared by dispersing the particles on a carbon-coated copper grid using acetone. Width and length of randomly selected one hundred particles were measured by handwork using the images.

Figure 1 shows the XRD patterns of the synthesized particles with the JCPDS PDF# 09-0432 for HAP. The pattern for AOT/Ca = 0 shows a HAP pattern without any other phases. The peaks in the patterns are not very sharp, which may be due to the small nm order particle size. The patterns for AOT/Ca ≠ 0 also show a HAP pattern, indicating that HAP particles are formed even if AOT is added into the reactant solution. The peaks become slightly sharper with increasing AOT/Ca, because the particle size becomes larger with increasing AOT/Ca as shown below. Figure 2 shows the STEM images. The HAP particles synthesized at AOT/Ca = 0 are small round-shaped or rod-shaped particles. In contrast, the HAP particles synthesized at AOT/

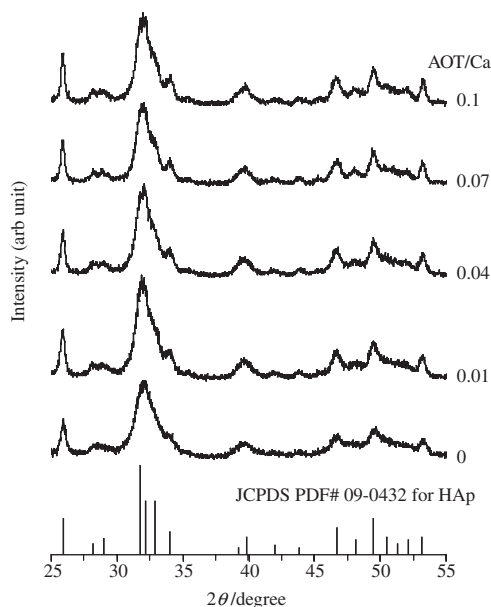


Figure 1. XRD patterns of the particles synthesized at various AOT/Ca ratios.

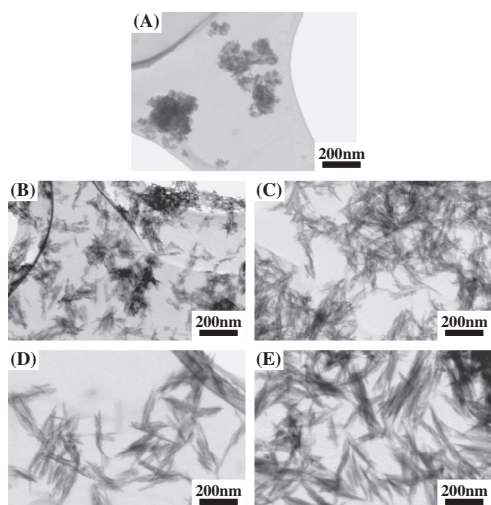


Figure 2. STEM images of the particles synthesized at AOT/Ca = 0 (A), 0.01 (B), 0.04 (C), 0.07 (D), 0.1 (E).

Ca \neq 0 are relatively larger rod-shaped particles. Figure 3 shows the width and the length. The width is approximately constant at 12 nm regardless of AOT/Ca, whereas the length increases from 40 to 100 nm with increasing AOT/Ca. The size and shape of the particles synthesized at AOT/Ca = 0.1 are similar to those obtained using AOT-base W/O microemulsions.^{7,8}

In fact, when the Ca(NO₃)₂ solution and the AOT solution were mixed together in the glass tube, the mixture was not transparent but turbid due to the Ca–AOT complex formed by an interaction between the positive charge of calcium ion and the negative charge of the polar headgroup of AOT. The Ca–AOT complex might play a key role in the rod-shaped HAp nanoparticle formation. Possible causes for the formation are proposed as follows. If the Ca–AOT complex is the starting

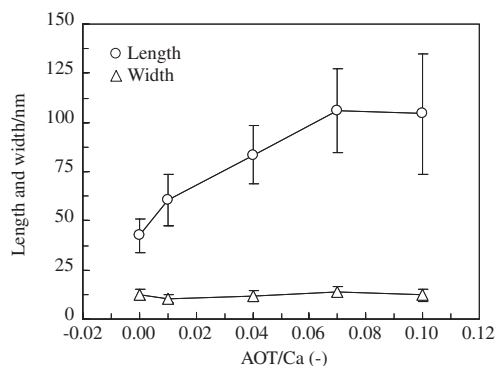


Figure 3. Length and width of the synthesized particles as a function of AOT/Ca.

material for calcium ions to synthesize HAp particles, the calcium must separate from the polar headgroup of AOT while avoiding interaction in order to react with phosphate ions. However, the interaction is so strong that particle nuclei formation might be slow. Then, Ostwald ripening occurs resulting in the larger-sized particle formation. The *ac* and *bc* particle faces (surface of the side wall of the rod-shaped HAp particles) are rich in calcium ions.¹⁵ Therefore, the polar headgroup of AOT interacts with the calcium ions, and the *ac* and *bc* particle faces have an AOT adsorption layer on it. The layer inhibits the particle growth on the *ac* and *bc* particle faces. Then the growth on the *ab* particle face (surface of the top and bottom wall of the rod-shaped HAp particles) is enhanced to form the longer particles. The length versus AOT/Ca in Figure 3 shows that the enhancement is more remarkable with increasing the amount of AOT.

In summary, rod-shaped HAp nanoparticles are formed using AOT and water. This indicates that an oil phase is not necessarily needed to form the rod-shaped HAp nanoparticles using AOT. The Ca–AOT complex might be the origin of the particles formation.

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