

## Formation of Hydroxyapatite Microtubes Assisted with Anatase under Hydrothermal Conditions

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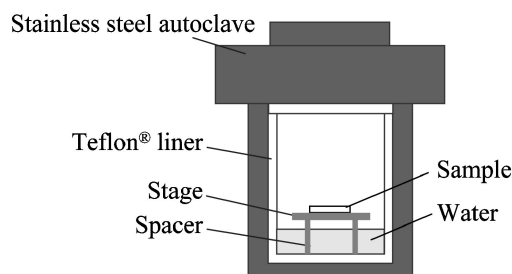
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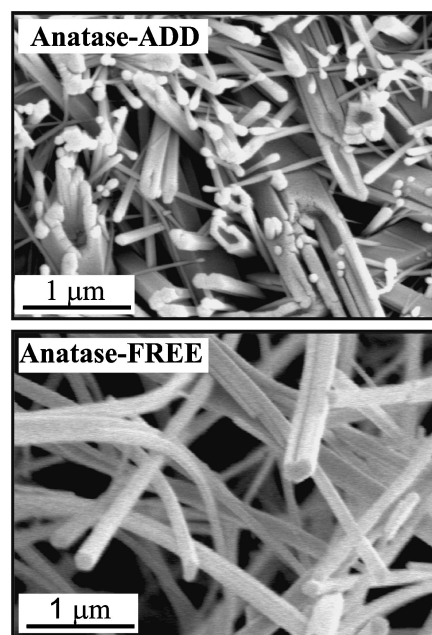
Hydroxyapatite (HA) has attracted much attention due to its biocompatibility and adsorption capability. The HA microtubes are highly attractive because they can provide improvement of functionality. It was found that HA microtubes were formed when  $\alpha$ -tricalcium phosphate ( $\alpha$ -TCP) was hydrothermally treated with addition of anatase. The fact that microtubes did not form under titania-free conditions indicated that titania played important roles to form microtubes.

Hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ; HA) is the main inorganic component of our bones and teeth. HA ceramics have been used as artificial bones and as chromatographic stationary phases due to its biocompatibility<sup>1</sup> and adsorption capability,<sup>2</sup> respectively. The properties of HA ceramics can be tailored by the size and morphology of particles constructing the ceramics. Preparation of HA particles with different morphologies, such as rod (or fiber)-like,<sup>3-6</sup> plate-like,<sup>7,8</sup> and tubular<sup>9</sup> shapes, has been reported. Among the morphologies, tubular shape is highly attractive because it can provide improvement of functionality because of their larger surface area and light weight. In a previous study,<sup>9</sup> HA microtubes were prepared in a mixed solvent of water/*N,N*-dimethylformamide by a solvothermal method. In the present paper, a new formation system for HA microtubes is described. *N,N*-Dimethylformamide used in the previous report is an organic solvent harmful to both our health and environment. The present system provides HA microtubes by using only water vapor without an organic solvent. Moreover, the use of water vapor would be an advantage of mass production because the collection of the products is easy and the waste heat from the factory is available.

We found the formation of HA microtubes when  $\alpha$ -tricalcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ;  $\alpha$ -TCP) was hydrothermally treated with addition of anatase. The HA microtubes were prepared as follows:  $\alpha$ -TCP powder (Taihei Chemical Industrial Co., Ltd., Japan) and anatase powder ( $\text{TiO}_2$ , ST-01, Ishihara Sangyo Kaisha, Ltd., Japan) were mixed in a mass ratio of 65:35 with a mortar. The mixed powder (0.05 g) was pressed to obtain a pellet 8 mm in diameter and 0.6 mm in thickness (Sample Anatase-ADD). As a reference, a pellet composed of only  $\alpha$ -TCP powder was also prepared by the same conditions (Sample Anatase-FREE). The specimens were set in a 50-cm<sup>3</sup> Teflon<sup>®</sup>-lined autoclave with 10 cm<sup>3</sup> of water. The autoclave was put into an oven kept at 120 °C, and the specimens were exposed to water vapor at 120 °C under saturated vapor pressure for 24 h. A schematic illustration is shown in Figure 1. This system is preferred for preparing rod-like HA particles from  $\alpha$ -TCP. After the hydrothermal treatment, the autoclave was cooled down by a blower at room temperature. The samples were taken out from



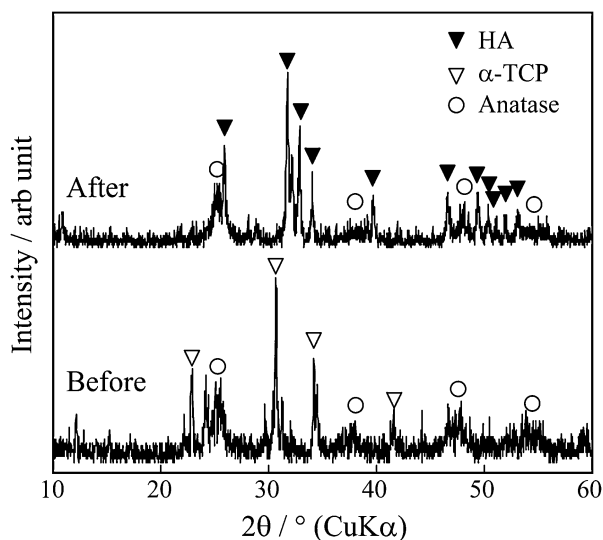
**Figure 1.** Schematic illustration of hydrothermal treatment.



**Figure 2.** SEM photographs of the samples Anatase-ADD and Anatase-FREE after the hydrothermal treatment.

the autoclave, washed with distilled water, and dried at 90 °C. The samples were analyzed by X-ray diffractometry (XRD; RINT-2200VL, Rigaku Corporation, Japan) and observed by scanning electron microscopy (SEM; S-4100, Hitachi Ltd., Japan).

Figure 2 shows SEM photographs of the samples Anatase-ADD and Anatase-FREE after the hydrothermal treatment. Many microtubes were found on the surface of the sample Anatase-ADD. On the other hand, only rod-like particles were observed on the surface of the sample Anatase-FREE.



**Figure 3.** XRD patterns of the sample Anatase-ADD before and after the hydrothermal treatment.

Figure 3 shows XRD patterns of the sample Anatase-ADD before and after the hydrothermal treatment. The diffraction lines ascribed to  $\alpha$ -TCP and anatase were detected before the hydrothermal treatment, while those ascribed to HA and anatase were detected after hydrothermal treatment. This indicates that  $\alpha$ -TCP changed to HA during treatment and anatase did not change. We previously reported that we can obtain rod-like HA particles by a hydrothermal treatment of  $\alpha$ -TCP.<sup>5,6</sup> In fact, the sample Anatase-FREE was composed of rod-like HA particles after the treatment. This indicates that the microtubes and rod-like particles observed on the surfaces of the samples were HA. HA microtubes were formed on the sample Anatase-ADD. Although the specimen was not in direct contact with liquid water in the autoclave, the water vapor was speculated to condense on the specimen and reacted with  $\alpha$ -TCP during treatment. Without assuming the existence of liquid water on the specimen, the crystal growth of HA is difficult to explain in such low temperature.

The anatase itself did not react with water or  $\alpha$ -TCP, but the morphology of the HA particles was affected by the presence of anatase. The formation mechanism of HA microtubes is still under investigation, but we speculated two possible effects of anatase. One is the effect on the nucleation of HA. Under the HA formation from  $\alpha$ -TCP, the dissolution of  $\alpha$ -TCP occurs at first, the condition where the supersaturation of HA is achieved, and

then HA nucleation occurs. It has been reported that anatase induces HA nucleation in a solution which is supersaturated with HA.<sup>10,11</sup> It can be speculated that the HA nucleation induced by anatase provided the formation of HA microtubes. The other possibility is the spatial effect. We also conducted the same hydrothermal treatment of pellets composed of  $\alpha$ -TCP and anatase powders with a mixing ratio different from 65:35, but HA microtubes were hardly formed in these cases. The added anatase particles might have affected the HA crystal growth and finally induced the formation of microtubes. The size of the obtained microtube was not so different from that reported in the previous study,<sup>9</sup> but cracks were observed along the long axis only on some of the present microtubes. The crack formation implies the inhomogeneous crystal growth on the microtubes in the present system. The advantage of the present method over the previous one<sup>9</sup> is that we can obtain the shaped materials composed of the HA microtubes.

The microtube structure of HA would be useful even when we considered the application of the present material as an HA/anatase nanocomposite for environmental purification because the microtube structure can provide large surface area.

The further investigation will provide the insights of HA crystal formation and production of HA microtubes.

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