Synthesis of *c* Axes Oriented Hydroxyapatite Aggregate

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The *c* axes oriented hydroxyapatite (HAp) aggregates were synthesized by the hydrolysis of $CaHPO_4 \cdot 2H_2O$ (DCPD) at 100 °C in 10 mass% NaOH solution. The HAp was of a plate-like form resembling DCPD. The X-ray diffraction pattern shows that the relative peak intensities of 002 and 004 diffractions increased with the temperature. The crystals in an aggregate were aligned perpendicular to the wide surface of an original plate-like DCPD. HAp crystallites grew in the [00l] direction perpendicular to the wide surface of plate-like HAp aggregate.

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) is the main inorganic component of hard tissues such as bone and teeth in human body and is also used for artificial bone,[1] liquid chromatographic packing[2] and scaffold for tissue engineering.[3] Therefore, it is important to control the surface reactivity of HAp by variation of morphology and aggregate form of the crystal. Many synthesis methods such as precipitation,[4] hydrothermal,[5] hydrolysis of salts[6–9] and sol-gel methods[10,11] have been known. However, there have been the only reports on the control of HAp crystal orientation, that is, Langmuir-Blodgett (LB)[12] and electrochemical deposition methods.[13] In the present paper, the synthesis of *c*-axes oriented HAp aggregates, obtained through the hydrolysis of $CaHPO_4 \cdot 2H_2O$ (DCPD), was reported.

The synthesis of HAp is based on the following reaction:

$$10CaHPO_4 \cdot 2H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 20H_2O + 10H^+ + 4PO_4^{3-}$$

Actually, the chemical composition (Ca/P atomic ratio) varies with preparation condition in aqueous solution from 1.50 to 1.67 such as $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x} \cdot nH_2O$, where $0 \leqq x \leqq 1$,[14] and the HAp structure can partially be replaced by other ions (e.g. Na^+, Mg^{2+} and CO_3^{2-} ions).[15]

The samples were prepared by the hydrolysis of 20 g DCPD (Reagent grade, Kanto Chemical) in 500 ml NaOH (Reagent grade, Kanto Chemical) aqueous solution (10–30 mass%). The morphology of DCPD was of a plate-like form and the average particle size was estimated to be 53 μm. The solutions were stirred slowly while the temperature was maintained between 25 and 100 °C. The precipitates obtained were filtered, and washed by distilled water. After drying at 100 °C, the crystal phase and composition of powders were determined by X-ray powder diffractometry (XRD, Philips PW1700), Fourier transform infrared spectrometer (FTIR, Perkin Elmer Spectrum2000) and energy disperse X-ray spectroscopy (EDS, JEOL JED-2200). The surface morphologies were observed by scanning electron microscopy (SEM, JEOL JSM-5600) and field emission scanning electron microscopy (FE-SEM, JEOL JSM-6330F). The average particle size was measured using particle size distribution analyzer (Shimudzu, SALD-2100). The specific surface area was measured by the BET (Shimadzu 2200) method.

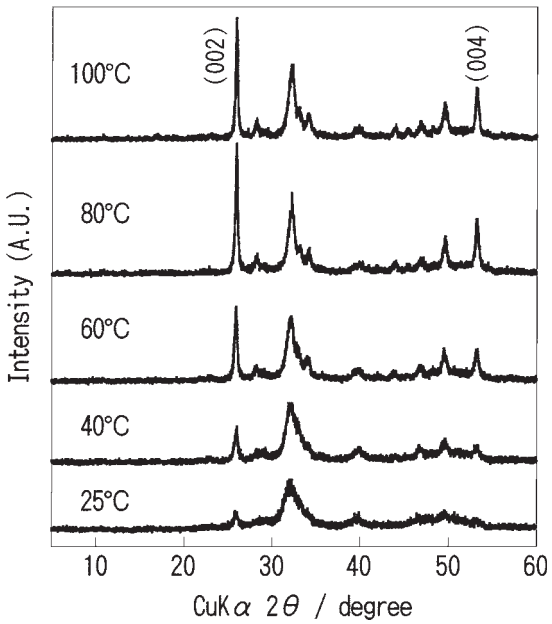

Figure 1. XRD patterns of HAp obtained by hydrolysis of DCPD at different temperatures in 10 mass% NaOH solution for 1 h.

From the XRD measurements, the powders obtained by the hydrolysis of DCPD were identified as low crystalline HAp. The phase conversion from DCPD to HAp was completely achieved within 30 min at 25 °C and 5 min at 100 °C. No intermediate compounds such as $CaHPO_4$ and $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$ were detected during the hydrolysis reactions at any temperature. From the EDS analysis, the small amount of sodium component was detected, assuming that the sodium ions were adsorbed on or incorporated into the low crystalline HAp.

According to FTIR spectra, the adsorption bands at 875, 1415 and 1468 cm^{-1} were assinable to the HAp containing carbonate ions. It is known that the CO_3 ions can replace both the OH site (A site) and the PO_4 site (B site) in the HAp structure. The CO_3 peaks of the powders were assigned to B-type carbonate HAp.

From the SEM observations, the powders synthesized in 10 mass% NaOH solution were of a plate-like form resembling DCPD. The average particle size was estimated to be 28 μm. The relative peak intensities of 002 and 004 diffractions increased with the temperature (Figure 1). For NaOH solutions more than 20 mass%, the powders were pulverized and agglomerated owing to the electrostatic repulsion of HAp particles in the solution decreased with increase in ionic strength.[16]

According to the FE-SEM observation, HAp powder,

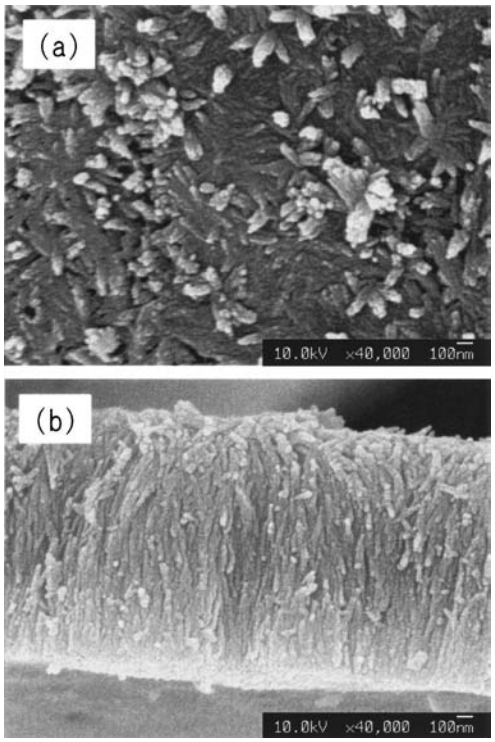

Figure 2. FE-SEM image of HAp surfaces; (a) Surface of HAp prepared at 25 °C in 10 mass% NaOH solution for 1 h; (b) Cross section of HAp prepared at 100 °C in 10 mass% NaOH solution for 1 h.

synthesized at 25 °C in 10 mass% NaOH, was composed of small crystals with random orientation [Figure 2(a)]. The crystallite size was estimated by XRD employing the Scherrer's equation, which was monotonously increased from a size of about 150 nm (002 reflection) × 190 nm (300 reflection) at 25 °C to 380 nm × 200 nm at 100 °C. In addition, the needle-like crystals were aligned perpendicular to the wide surface of an original plate-like DCPD as shown in Figure 2(b). The specific surface area increased from 50 m^2/g (25 °C) to 91 m^2/g (100 °C).

From the results of FE-SEM observation and XRD measurement, the HAp crystals grew in the [00l] direction perpendicular to the wide surface of plate-like HAp aggregate. For this reason the formation of oriented HAp is considered to be initiated by the heterogeneous nucleation of HAp on DCPD surface and subsequently, the crystal growth of the [001] direction is promoted by the rapid dissolution-precipitation reaction at high temperature.

The thermal stability of oriented HAp was also investigated. The phase composition and alignment characteristic of HAp were maintained after heating at 750 °C for 1 h (Figure 3). However, the decomposition of HAp into a mixture of HAp and β-$Ca_3(PO_4)_2$ was observed after heating at 1000 °C for 3 h. Therefore, the synthesized HAp at 100 °C in 10 mass% NaOH solution was indicated to be a calcium deficient hydroxyapatite having Ca/P atomic ratio less than 1.67.[4]

In summary, the aggregate of HAp needle-like crystallites, whose *c* axes were well oriented, was synthesized by the hydrolysis of DCPD at 100 °C in 10 mass% NaOH solution. It is expected that the oriented powder is useful to elucidate surface-dependent biological reactivity.

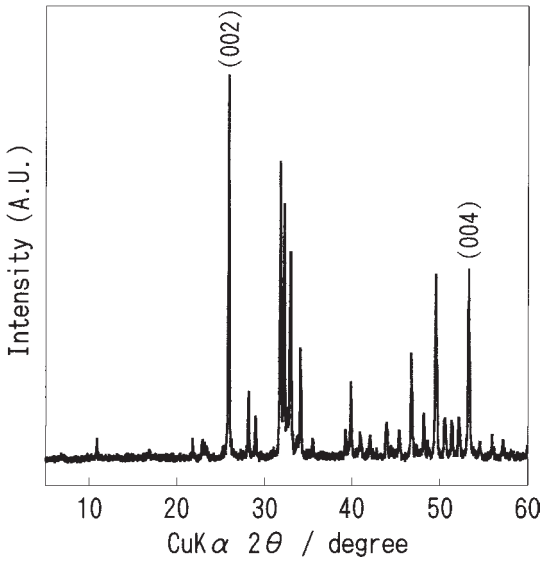

Figure 3. XRD pattern of oriented HAp aggregate obtained through hydrolysis of DCPD at 100 °C in 10 mass% NaOH solution for 1 h and then after heating at 750 °C for 1 h.

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