Formation of needle-like hydroxyapatite by hydrothermal treatment of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ combined with $\beta\text{-Ca}_3(\text{PO}_4)_2$

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Conditions were investigated for preparing needle-like hydroxyapatite (HAp; $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) by hydrothermal processing of mixed calcium phosphate powders consisting of dicalcium phosphate dihydrate (DCPD; $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) and beta-tricalcium phosphate ($\beta\text{-TCP}$; $\beta\text{-Ca}_3(\text{PO}_4)_2$). The powder mixture was subjected to two-step hydrothermal processing in which the compacted powder was treated first by exposure to vapor of the liquid and subsequently by immersion in the liquid. High aspect ratios were obtained in samples with crystal sizes around $60\text{ }\mu\text{m}$ in length from the reactant mass ratio composition of $\beta\text{-TCP}/\text{DCPD} = 1/9$ by treatment at 160°C for 0.5 h under vapor conditions, followed by liquid conditions for 24 h with renewal of the liquid at 12 h. Initial compositions and pH conditions were the main parameters determining the formation of needle-like HAp by hydrothermal processing.

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1. Introduction

Hydroxyapatite (HAp; $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is known to have high biological affinity, such as osteoconductivity when it is implanted in the body,^{1,2)} and hence is widely used as an artificial substitute in the repair of bone tissues. Another popular application of HAp is as column packing for liquid chromatography because of HAp's adsorption characteristics for proteins.^{3,4)} Protein adsorption on HAp crystals is governed by the physicochemical properties of the crystals that are influenced by the size, morphology and pore structure of the HAp phase. HAp has two typical crystal faces, namely the *a*-face and the *c*-face. The *a*-face of HAp has a positively charged site composed of two screw-axis Ca ions, while the *c*-face has a negatively charged site coordinated to oxygen ions belonging to three phosphate ions.^{5,6)} The unique characteristics of the different crystal faces of HAp allow separation of proteins. Because of the dependence of these characteristics on the surfaces, it is worth investigating synthetic procedures for rod-shaped or needle-shaped crystals with high aspect ratios. Micrometer-sized crystals of HAp with high aspect ratios are required because large HAp crystals are suitable for easy characterization by protein adsorption.

Among the procedures for synthesis of HAp, hydrothermal processing interests us as it allows easy fabrication of micrometer-sized rod-shaped crystals below 200°C .^{7,8)} Ioku et al. fabricated rod-shaped HAp through hydrothermal processing in which compacted alpha-tricalcium phosphate ($\alpha\text{-TCP}$; $\alpha\text{-Ca}_3(\text{PO}_4)_2$) was exposed to hydrothermal vapor.⁹⁾ Using their process, compacted powder of $\alpha\text{-TCP}$ was completely transformed to calcium-deficient HAp after treatment for 3 h at 120°C or more. The synthesized HAp was an agglomeration of rod-shaped crystals,

with an approximate length of $20\text{ }\mu\text{m}$ and aspect ratio of about 10, locked together to make micrometer-sized pores. Previous work also showed that whiskers of HAp crystals could be formed by hydrothermal treatment of beta-tricalcium phosphate ($\beta\text{-TCP}$; $\beta\text{-Ca}_3(\text{PO}_4)_2$) with citric acid.¹⁰⁾ During this process, compacted powder of the initial calcium phosphate was immersed. We regard the treatment of calcium phosphate with a solution vapor as a treatment requiring much less solution than immersion in the solution. Rapid reaction of the calcium phosphate substrate with less solution leads to more rapid precipitation at the particle surface and better adhesion of the particle. Therefore, treatment of calcium phosphate using vapor can result in adhesion among the particles that results in the compacted powder being fixed, even if it is composed of highly soluble calcium phosphate, but the problems of inhomogeneous transformation remain. On the other hand, immersion of the compacted calcium phosphate will produce homogeneous phases through rapid reactions with surrounding solution but hydrothermal treatment using liquid sometimes makes the compacted powder collapse when the initial calcium phosphate dissolves in the solution. Hence, we expect that hydrothermal treatment using a vapor followed by a liquid would enable us to form pellets of homogeneous calcium phosphate, even if they were prepared from highly soluble calcium phosphate. Thus, we are interested in the process whereby samples are immersed in liquid after exposure to liquid vapor, under hydrothermal conditions.

From these viewpoints, the present study was conducted to investigate conditions for the fabrication of needle-shaped crystals with high aspect ratio through hydrothermal processing, starting from highly soluble dicalcium phosphate dihydrate (DCPD; $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). The combined process of exposure to solution vapor followed by immersion in the solution is hereafter called "two-step hydrothermal processing." We expect that two-

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step hydrothermal processing may maintain the form of the initial compacted powder, even when the pellets contain highly soluble calcium phosphates such as DCPD. However, the relationships between synthetic conditions and morphology of the HAp crystals formed have not been clarified for two-step hydrothermal processing of compacted powder consisting of calcium phosphates. In the present study, we report synthetic conditions for needle-shaped HAp produced by two-step hydrothermal processing of compacted powder composed of DCPD with added β -TCP. DCPD, with higher solubility than α -TCP, was able to transform to HAp by hydrothermal vapor treatment. β -TCP was used as a reactant that leads to continuous crystal growth after immersion in the hydrothermal liquid because of its relatively low solubility. Specifically, DCPD is expected to maintain the form of the pellet during transformation, while β -TCP acts as a reactant for crystal growth in the water. The crystalline phases and their morphologies in the products were characterized to discuss the feasibility of increasing the size of the HAp crystals formed through two-step hydrothermal processing.

2. Experimental procedure

Table 1 shows preparation conditions including initial compositions, the ratios of treatment solution volumes to initial material weights, treatment temperatures and liquid exposure periods. Pellets of the initial powders were prepared by mixing the reactants DCPD (Wako Pure Chemical Industries, Ltd., Japan) and β -TCP (Taihei Chemical Industrial Co., Ltd., Japan) in several different ratios so that β -TCP/DCPD = 10/0, 3/1, 1/1, 1/3, 1/9 and 0/10 by mass. Amounts of 0.4 or 0.2 g of the mixed powder were compacted into a cylindrical shape under a pressure of 1×10^8 Pa. The powder pellets were treated hydrothermally in a designed vessel (Shikoku Rika Co.), as shown in **Fig. 1**. Specimens of the compacted powder were placed in a 100 cm³ autoclave with 20 cm³ of $\text{NH}_4\text{Cl} / \text{NH}_3$ buffer solution with an NH_4Cl concentration of 2 mol·dm⁻³ at pH 7.3. Maintenance of the pH of the buffer solution was confirmed even after the hydrothermal treatment without coexistence of calcium phosphates. Samples were first exposed hydrothermally to the vapor phase at 140, 160 or 180°C for 0.5 h (“vapor conditions”), followed by immersion in the liquid phase at the same temperature (“liquid conditions”), by turning over the vessel. After liquid conditions in the vessel had been maintained for 24 h, the vessel was cooled to room

temperature, and the specimens were taken out of the vessel. In one instance, the solution in the vessel was renewed after the sample had been immersed for 12 h, and the sample was soaked for a further 12 h (12 + 12 h). The obtained specimens were rinsed with ultrapure water, and dried in air at 100°C. The pH values of the solutions after hydrothermal treatment were measured using a pH meter.

The phases produced in the specimens were identified by powder X-ray diffraction (XRD; RINT 2100HL, Rigaku Co.) using $\text{Cu K}\alpha$ radiation, operating at 40 kV and 20 mA. The International Center for Diffraction Data (ICDD) database was used in a search and match program for phase identification. The morphology of specimens was observed under a scanning electron microscope (SEM; JSM-5600, JEOL Ltd.) at 15 kV. Ca/P atomic ratios in the synthesized specimens were estimated by the relative X-ray intensity of peaks between β -TCP and HAp phases, according to methods previously reported.¹¹⁾ Determination of Ca/P ratios by XRD is available as an alternative method for estimation of nonstoichiometric HAp.¹²⁾ In addition, Ioku et al. reported that the determined Ca/P atomic ratios were almost same values determined by chemical analysis with inductively coupled plasma spectroscopy for the rod-shaped HAp.⁹⁾ Hence, it is worth describing the method briefly for the estimation of Ca/P atomic ratio. In this method, the Ca/P atomic ratio was estimated by the equation:

$$\text{Ca/P} = (10A_h + 3A_b) / (6A_h + 2A_b)$$

where A_h and A_b are the areas of peaks at $2\theta = 31.8^\circ$ ($d = 0.281$ nm, $100, 2\ 1\ 1$) for HAp and at $2\theta = 31.0^\circ$ ($d = 0.288$ nm, $100, 0\ 2\ 10$) for β -TCP, respectively, in the powder XRD patterns of samples that were decomposed in air for 3 h at 900°C.

3. Results

Figure 2 shows the powder XRD patterns and SEM images for samples synthesized from compacted powder with a composition of β -TCP/DCPD = 10/0 and 0/10, that is, pure β -TCP and DCPD as reference materials. The synthesis temperature was 160°C, because that temperature is in the middle of the range that was reported to produce HAp from α -TCP under vapor conditions (120°C) and β -TCP under liquid conditions (200°C), respectively. Major peaks in the XRD patterns were assigned according to PDF#9-432 for hydroxyapatite (HAp), PDF#75-1520 for monetite (dicalcium phosphate anhydrous, DCPA; CaHPO_4) and PDF#9-169 for whitlockite (β -TCP). The XRD patterns of the samples show that β -TCP was completely transformed to HAp phases while DCPD was transformed to HAp and DCPA. Rod-shaped crystals 5–20 μm in length were observed on

Table 1. Synthetic Conditions

No.	Initial composition		Temperature	Powder / liquid ratio	Periods for exposure to the liquid
	β -TCP/DCPD ^a in mass ratio	Ca/P atomic ratio			
1	10 / 0	1.50	160°C	0.4 g / 20 cm ³	24 h
2	0 / 10	1.00	160°C	0.4 g / 20 cm ³	24 h
3	3 / 1	1.38	160°C	0.4 g / 20 cm ³	24 h
4	1 / 1	1.26	160°C	0.4 g / 20 cm ³	24 h
5	1 / 3	1.14	160°C	0.4 g / 20 cm ³	24 h
6	1 / 9	1.05	160°C	0.4 g / 20 cm ³	24 h
7	1 / 9	1.05	140°C	0.4 g / 20 cm ³	24 h
8	1 / 9	1.05	180°C	0.4 g / 20 cm ³	24 h
9	1 / 9	1.05	160°C	0.2 g / 20 cm ³	24 h
10	1 / 9	1.05	160°C	0.2 g / 20 cm ³	12 + 12 h ^b

^a β -TCP: $\text{Ca}_3(\text{PO}_4)_2$, DCPD: $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$

^bLiquid was renewed after the treatment for 12 h, followed by further treatment for 12 h.

Fig. 1. Apparatus for hydrothermal treatment under (a) vapor conditions and (b) liquid conditions.

Fig. 2. Powder XRD patterns (left) and SEM images (right) of samples prepared by hydrothermal treatment of compacted powder of β -TCP or DCPD. Hydrothermal treatment was carried out at 160°C under vapor conditions for 0.5 h, followed by liquid conditions for 24 h. The total mass of calcium phosphates was 0.4 g for each vessel.

Fig. 3. HAp content formed in the compacted powder, starting from β -TCP or DCPD, after hydrothermal treatment under liquid conditions for various periods. The amount of HAp formed was determined from relative peak intensities of peaks at $2\theta = 31.8^\circ$ ($d = 0.281$ nm, $I_{100}, 2\ 1\ 1$) for HAp and at $2\theta = 31.0^\circ$ ($d = 0.288$ nm, $I_{100}, 0\ 2\ 10$) for β -TCP in XRD patterns for compacted powder starting from β -TCP, as well as peaks at $2\theta = 31.8^\circ$ ($d = 0.281$ nm, $I_{100}, 2\ 1\ 1$) for HAp and at $2\theta = 30.2^\circ$ ($d = 0.296$ nm, $I_{81}, 1\ 2\ 0$) for DCPA in XRD patterns for compacted powder starting from DCPD.

the specimens starting from β -TCP. In contrast, the surfaces of specimens starting from DCPD had small needle-like particles less than 5 μ m in size. After the liquid hydrothermal treatment, the specimen obtained from DCPD had enough mechanical strength for handling by tweezers without significant breakage, whereas that from pure β -TCP was easily broken after the same handling. The improved strength for handling was caused by chemical reactions occurring during hydrothermal processing. The pH values of the solutions after hydrothermal treatment of β -TCP and DCPD were 6.8 and 4.0, respectively.

Figure 3 shows the contents of the HAp formed in the compacted powder starting from β -TCP and DCPD, after hydrothermal treatment under liquid conditions for various periods. The conversion ratios from β -TCP and DCPA were determined by measuring the relative intensities of peaks at $2\theta = 31.8^\circ$ ($d = 0.281$ nm, $I_{100}, 2\ 1\ 1$) for HAp and $2\theta = 31.0^\circ$ ($d = 0.288$ nm, $I_{100}, 0\ 2\ 10$) for β -TCP, in XRD patterns for compacted powder starting from β -TCP, as well as the intensities of peaks at $2\theta = 31.8^\circ$ ($d = 0.281$ nm, $I_{100}, 2\ 1\ 1$) for HAp and $2\theta = 30.2^\circ$ ($d = 0.296$ nm, $I_{81}, 1\ 2\ 0$) for DCPA in XRD patterns for powder

pellets starting from DCPD. After treatment under liquid conditions for 1 h, β -TCP and HAp were detected in XRD patterns of the pellets starting from β -TCP, while DCPA was detected on those from DCPD. This means that DCPD can easily convert to DCPA during hydrothermal processing. The amounts of HAp formed increased more rapidly for the sample starting from β -TCP than that starting from DCPD. Almost all of the β -TCP was transformed to HAp within 6 h after hydrothermal treatment under liquid conditions. In contrast, about 60 mass% of HAp was formed and 40 mass% of DCPA remained when the compacted DCPD powder was treated hydrothermally for 12 h. The rate of transformation from DCPA to HAp was distinctly slower than from β -TCP.

Figure 4 shows powder XRD patterns and SEM images of the samples synthesized through hydrothermal treatment of mixed powders consisting of β -TCP and DCPD at various β -TCP/DCPD mass ratios of 3/1, 1/1, 1/3 and 1/9, with 0.4 g total mass of initial powder in each vessel. The specimens shown in Fig. 4 were synthesized at a temperature of 160°C under vapor conditions for 0.5 h, followed by liquid conditions for 24 h. The XRD pattern of the specimen starting from β -TCP/DCPD = 3/1 showed that all peaks could be assigned to the HAp phase. Peaks assigned to DCPA were detected with increasing amounts of DCPD in the initial mixture. The amounts of DCPA formed increased with increasing amounts of DCPD in the compacted powder. All of the observed particle morphologies among the formed particles appeared to be needle-shaped, not only larger than the particles formed on the samples of the pellets starting from DCPD alone, but also with higher aspect ratios than particles formed from β -TCP alone. The pH values decreased with increasing DCPD concentration in the initial composition. After the hydrothermal treatment, while the specimen obtained from pure β -TCP was easily broken during handling by a tweezers, the specimens obtained from mixture composed of β -TCP and DCPD were strong enough to handle, even if it is composed of β -TCP and DCPD with β -TCP/DCPD mass ratio = 3/1.

Figure 5 shows powder XRD patterns and SEM images of samples prepared by hydrothermal treatment of mixed powder consisting of β -TCP and DCPD at various temperatures of 140, 160 or 180°C. Hydrothermal treatment was carried out on the specimen with β -TCP/DCPD mass ratio = 1/9 under vapor con-

Fig. 4. Powder XRD patterns (left) and SEM images (right) of samples prepared by hydrothermal treatment of mixed powder consisting of β -TCP and DCPD with β -TCP/DCPD mass ratios of 3/1, 1/1, 1/3 and 1/9. Hydrothermal treatment was carried out at 160°C under vapor conditions for 0.5 h followed by liquid conditions for 24 h. The total mass of calcium phosphates was 0.4 g for each vessel.

Fig. 5. Powder XRD patterns (left) and SEM images (right) of specimens prepared by hydrothermal treatment of mixed powder consisting of β -TCP and DCPD at temperatures of 140, 160 or 180°C. Hydrothermal treatment was carried out on the specimen with β -TCP/DCPD mass ratio of 1/9 under vapor conditions for 0.5 h followed by liquid conditions for 24 h. The total mass of calcium phosphates was 0.4 g for each vessel.

ditions for 0.5 h, followed by liquid conditions for 24 h. The total mass of the calcium phosphates was 0.4 g. Lower temperatures during hydrothermal processing produced larger amounts of DCPA in the specimens, although all specimens displayed sufficient strength for handling after the hydrothermal treatment. This means that the treatment temperature of the examined compacted powder did not influence the rate of transformation from DCPD to DCPA significantly, but did influence the rate of transformation from DCPA to HAp. The pH value decreased with increasing reaction temperature.

Figure 6 shows powder XRD patterns and SEM images of specimens prepared using different amounts of the compacted powder (β -TCP/DCPD = 1/9) after 24 h with the buffer solution at 160°C. The amounts of DCPA in the samples decreased with decreasing amounts of compacted powder under the same volume of buffer solution. The amount of DCPA also decreased

because of the renewal of the buffer solution. This means that larger amounts of solution in contact with the powder allowed complete formation of HAp under hydrothermal conditions. Higher aspect ratios were obtained by treatment of 0.2 g of the compacted powder and renewing the buffer solution.

The lengths and aspect ratios of the particles determined from SEM images are summarized in **Table 2**. The estimated Ca/P atomic ratios determined using the powder XRD methods are also given in Table 2. The length of the prepared sample was around 60 μm for the specimen prepared using 0.2 g of powder of composition β -TCP/DCPD = 1/9 and treatment at 160°C for 24 h with renewal of the buffer solution. This sample showed the highest aspect ratio and highest Ca/P atomic ratio among the samples prepared in this study. Larger amounts of solution in contact with the powder and renewal of the buffer solution minimized decreases in pH.

Fig. 6. Powder XRD patterns (left) and SEM images (right) of samples prepared by hydrothermal treatment of mixed powder consisting of β -TCP and DCPD with a total mass of 0.2 or 0.4 g in each vessel. Hydrothermal treatment was carried out under vapor conditions for 0.5 h followed by liquid conditions for 24 h, or liquid conditions for 24 h with renewal of the liquid at 12 h (denoted as 12 + 12 h). Hydrothermal treatment was carried out at 160°C for the specimen with β -TCP/DCPD mass ratio of 1/9.

Table 2. Summary of the Phases and Ca/P Atomic Ratios of the Obtained Calcium Phosphate, Determined by Powder XRD and the Length and Aspect Ratio of the Crystals Observed Under SEM

No.	Crystalline phase	Ca/P atomic ratio	Length (μm)	Aspect ratio	pH value of solution
1	HAp	1.64	5–20	11 $\pm$ 8	6.8
2	HAp and DCPA	1.54	1–2	n.d.	4.0
3	HAp	1.64	10–30	25 $\pm$ 8	5.5
4	HAp and DCPA	1.64	10–35	39 $\pm$ 12	4.7
5	HAp and DCPA	1.60	15–40	32 $\pm$ 12	3.4
6	HAp and DCPA	1.55	10–30	36 $\pm$ 8	3.8
7	HAp and DCPA	1.57	15–20	17 $\pm$ 3	5.0
8	HAp and DCPA	1.60	10–40	26 $\pm$ 7	3.2
9	HAp and DCPA	1.63	15–50	44 $\pm$ 17	4.9
10	HAp	1.65	20–60	45 $\pm$ 24	5.9

HAp: hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), DCPA: monetite (CaHPO_4).
n.d.: not determined.

4. Discussion

The compacted powder of DCPD alone was able to provide an increase in strength after hydrothermal treatment under vapor conditions and liquid conditions, while that of β -TCP alone did not. The transformation of DCPD to DCPA was able to proceed under vapor conditions while β -TCP was hardly converted to HAp. Therefore, the conversion of DCPD to DCPA contributed sufficient strength to allow handling of the compacted powder. The rate of transformation of DCPA to HAp, however, was lower than that of β -TCP to HAp under liquid conditions, as shown in Fig. 3. The transformation of DCPA to HAp gradually proceeded through the reaction (written as stoichiometric formula):

under liquid conditions. In contrast, the transformation of β -TCP to HAp occurred through the reaction (written as stoichiometric

formula):

after exposure to the liquid. Comparing the reactions of β -TCP and DCPA to form HAp, the larger amount of phosphoric acid produced from DCPA results in lower pH values. The lower pH of the surrounding solution reduces the rate of HAp formation, although the solubility of β -TCP is lower than that of DCPA at around pH = 7.

After hydrothermal treatment of β -TCP alone to form HAp, the resulting HAp had rod-shaped crystals, as shown in Fig. 2. The higher solubility of DCPD or DCPA allows many nuclei of HAp to be induced but nucleation of HAp from DCPA was accompanied by the falling pH of the local fluid around the nuclei preventing crystal growth by decreasing the degree of supersaturation with respect to HAp. In contrast, β -TCP was allowed to grow after immersion in the liquid, while little reaction could happen under vapor conditions. Mixing DCPD with β -TCP allowed the pellets to harden enough to be handled after vapor treatment, with possible formation of DCPA and nucleation of HAp. Following the vapor treatment, HAp nuclei grew to form needle-shaped HAp. The high aspect ratio of the needle-shaped crystals was maintained in the specimens in which the pellets had β -TCP/DCPD mass ratios from 3/1 to 1/9. Thus formed bulk structure has an advantage on usage for application where bulk form is used such as adsorbent with a unique characters derived from the needle-shape crystals. When compacted powder with initial β -TCP/DCPD compositions from 3/1 to 1/3 was treated hydrothermally, the HAp formed increased in size with increasing DCPD concentration in the initial material because a large amount of DCPA, which is used for crystal growth, was formed. Larger amounts of DCPD in initial material required longer periods and higher temperatures under neutral conditions to complete the formation of HAp, because the transformation of DCPA to HAp is slower than the transformation of β -TCP, as described in the results shown in Fig. 3, and DCPA is stable in the acidic region.

Supposing that the HAp formed after hydrothermal processing has a stoichiometric composition with atomic ratio Ca/P = 1.67

Table 3. Estimated Ratios of the Hydrothermally Prepared Specimens

No.	Calculated constituent of the phases (mass%)	
	HAp	DCPA
1	96.7	3.3
2	94.0	16.0
3	96.7	3.3
4	96.7	3.3
5	91.7	8.3
6	85.3	14.7
7	87.9	12.1
8	91.7	8.3
9	95.5	4.5
10	98.0	2.0

The estimated values were calculated on the basis of assumption where the hydroxyapatite (HAp, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and monetite (DCPA, CaHPO_4) have stoichiometric composition.

and DCPA has $\text{Ca/P} = 1.00$, the ratios of the constituents were determined as shown in **Table 3**. For the Ca/P atomic ratios of 1.64 and 1.65 in Table 2, the amounts of DCPA are estimated to be 3.3 and 2.0 mass%, respectively. Hence, the incomplete transformation of DCPA in compacted powder after hydrothermal processing is reflected in the difference between measured Ca/P and stoichiometric ($\text{Ca/P} = 1.67$) atomic ratios. The degree of transformation of DCPA in the compacted powder increased as the ratio of the mass of the compacted powder to the volume of the buffer solution decreased. The complete transformation was also enhanced by renewal of the buffer solution during hydrothermal processing.

A previous study reported that needle-shaped HAp was easily fabricated from DCPD under hydrothermal conditions at 220°C .¹³⁾ HAp with higher aspect ratio was obtained at lower temperatures than the previous report by addition of $\beta\text{-TCP}$. Our method provides HAp showing higher aspect ratio and higher Ca/P atomic ratio than that proposed by Ioku et al.,⁹⁾ while two-step hydrothermal processing was applied to the mixture of DCPD and $\beta\text{-TCP}$. The reactions on DCPD and $\beta\text{-TCP}$ completed to form HAp under an appropriate condition from the results of X-ray diffraction patterns. Formation of needle-shaped HAp crystals could be achieved by nucleation of HAp from DCPA and subsequent growth supplemented by ions from $\beta\text{-TCP}$

under neutral pH. The aspect ratio of the HAp crystals increased as the mass of reactants decreased and with renewal of the buffer solution. These preparation conditions allow the pH to remain neutral during the treatment under liquid conditions.

5. Conclusions

Needle-like HAp crystals were prepared hydrothermally by a two-step process utilizing vapor conditions for 0.5 h and subsequently liquid conditions for 24 h. DCPD in the pellets was transformed rapidly under vapor conditions into DCPA, which then transformed slowly into HAp under liquid conditions. High aspect ratios in samples with larger crystal sizes around $60\ \mu\text{m}$ in length were obtained from the reactant mass ratio composition of $\beta\text{-TCP/DCPD} = 1/9$ by treatment at 160°C for 0.5 h under vapor conditions followed by liquid conditions for 24 h, with renewal of the liquid at 12 h. Initial compositions and pH conditions were the main parameters determining the formation of needle-like HAp through hydrothermal processing.

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