

Preparation of hydroxyapatite porous ceramics with different porous structures using a hydrothermal treatment with different aqueous solutions

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Hydroxyapatite (HA) porous ceramics are useful for bone regeneration because HA shows a bone-bonding capability. The preparation of HA porous ceramics with controlled pore structures was attempted using a hydrothermal treatment of porous ceramics consisting of alpha tricalcium phosphate (α -TCP). The α -TCP porous ceramics were hydrothermally treated with various aqueous solutions containing NaCl, CaCl_2 , Na_3PO_4 , Na_2HPO_4 , NaH_2PO_4 , or H_3PO_4 at 150°C for a period of 10 h. The α -TCP phase of the porous ceramics was transformed into HA by the hydrothermal treatment in ultrapure water, NaCl, CaCl_2 , Na_3PO_4 or Na_2HPO_4 solutions, to form porous ceramics consisting of rod-shaped HA particles. The size of the rod-shaped HA particles prepared in Na_3PO_4 or Na_2HPO_4 solutions was smaller than that prepared in ultrapure water, NaCl, or CaCl_2 solutions. The α -TCP phase of the porous ceramics was transformed into a biphasic consisting of HA and monetite (DCPA) after treatment in NaH_2PO_4 solution, and into DCPA in the H_3PO_4 solution, resulting in porous ceramics consisting of plate-shaped particles. These results indicate that we could control the size and shape of the HA particles using the hydrothermal conditions, and this also provides a way of controlling the porous structure of the HA porous ceramics.

Key-words : Hydroxyapatite, Tricalcium phosphate, Hydrothermal treatment, Pore structure, Morphology

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1. Introduction

Our body is supported by bone, and bone plays an important role in our life. When a disease or an accident damages bone, the quality of life is significantly decreased. When the amount of damaged bone tissue is relatively small, then the damaged bone can spontaneously repair itself through a self-reconstructing capability. However, when the amount of damaged bone is too large for self-reconstruction, then the loss of bone may lead to the loss of function of related tissues. In such cases, implantation of artificial scaffolds that can support bone regeneration is one of the major treatments used.

Hydroxyapatite (HA , $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is the inorganic component of bone.⁽¹⁾ HA porous ceramics are useful scaffolds for bone regeneration because HA shows a bone-bonding capability, i.e., osteoconductivity.^{(2)–(4)} In the design of HA porous ceramics for bone regeneration, it is important to control their pore structures.^{(5),(6)} Pore structures can be designed using the size and morphology of the HA particles that are used to construct these porous ceramics. Ioku et al.^{(7)–(9)} reported that the hydrothermal method allows for the production of rod-shaped HA single crystals and porous ceramics consisting of rod-shaped HA. We expect that HA porous ceramics with a controlled pore structure can be obtained using a hydrothermal treatment of alpha tricalcium phosphate (α -TCP, $\text{Ca}_3(\text{PO}_4)_2$) porous ceramics having a controlled pore structure, because the initial pore structure influences the final structure. The inherent structure remains when such HA porous ceramics are produced from coral skeleton using a hydrothermal

treatment.⁽¹⁰⁾ The characteristics of the resultant HA particles, such as their size and morphology, are determined by the experimental conditions, especially the type of solution used during the hydrothermal treatments. Yoshimura et al.⁽¹¹⁾ reported that the addition of KOH, K_3PO_4 , and EDTA was effective in controlling the aspect ratio of HA. Nagata et al. reported that the addition of methanol⁽¹²⁾ or ethylamine⁽¹³⁾ was effective in controlling the morphology of HA particles. However, the effect of the type of solution used in the preparation of HA using a hydrothermal treatment has not been widely reported in detail so far.

The purpose of this study was to investigate the effect of the type of solution used in the hydrothermal treatment of α -TCP porous ceramics with 80% continuous pores around 10–50 μm in size.

2. Experimental procedure

2.1 Preparation of the α -TCP porous ceramics

α -TCP porous ceramics having a porosity of 80% with interconnecting pores with a diameter of 10–50 μm were prepared by following the method in a previous report.⁽¹⁴⁾ A mass of 20 g of β -TCP (Nacalai Tesque Inc., Japan), 20 g of potato starch (Nacalai Tesque Inc., Japan), and 35 g of ultrapure water were mixed to form a slurry. The slurry was poured into an alumina crucible and dried at 60°C overnight. After drying, the slurry was heated to $1,000^\circ\text{C}$ for a period of 3 h to burn out the starch, and then the product was sintered at $1,400^\circ\text{C}$ for a period of 12 h to obtain an α -TCP porous ceramic.

Table 1. Sample Notations and Used Aqueous Solutions

Notation	Solution
UPW	Ultrapure water (No additive)
NC	0.1 mol·dm ⁻³ NaCl
0.1CC	0.1 mol·dm ⁻³ CaCl ₂
1CC	1.0 mol·dm ⁻³ CaCl ₂
N3P	0.1 mol·dm ⁻³ Na ₃ PO ₄
N2HP	0.1 mol·dm ⁻³ Na ₂ HPO ₄
NH2P	0.1 mol·dm ⁻³ NaH ₂ PO ₄
H3P	0.1 mol·dm ⁻³ H ₃ PO ₄

2.2 Hydrothermal treatment

Two α -TCP porous ceramic samples with dimensions of about $5 \times 5 \times 5$ mm³ were placed in a 100 cm³ sealed vessel with either 20 cm³ of ultrapure water or various aqueous solutions containing NaCl, CaCl₂, Na₃PO₄, Na₂HPO₄, NaH₂PO₄, or H₃PO₄. The sample notations and the solutions used are given in **Table 1**. The reagents used to prepare these solutions were purchased from Nacalai Tesque Inc. (Japan). The sealed vessel was heated to 150°C for a period of 10 h for the hydrothermal treatment. After the treatment, the samples were removed, washed with ultrapure water, and dried at 60°C.

2.3 Characterization

The product was characterized using X-ray powder diffraction (XRD, RINT2200V/PC-LR, Rigaku, Japan), and the morphology of the product was observed using scanning electron microscopy (SEM, S-4800, Hitachi, Japan). A thin layer of gold was coated on the surface of the product to carry out the SEM observations.

3. Results

3.1 Hydrothermal treatment in ultrapure water, NaCl, and CaCl₂ solutions

Figure 1 shows the XRD patterns of the samples before and after the hydrothermal treatment in ultrapure water, NaCl, and CaCl₂ solutions. The phase of the sample before treatment was identified as being α -TCP (PDF No. 09-0348). The phase of the samples was transformed from α -TCP to monophase HA (PDF No. 09-0432) for Samples UPW, NC, 0.1CC, and 1CC. However, a shift in the peaks was observed for Samples NC, 0.1CC, and 1CC, compared to Sample UPW. The peak shift increased in the order: NC < 0.1CC < 1CC. This was due to the incorporation of chloride ions into the HA, because the lattice parameters were approached to those of chlorapatite (PDF No. 33-0271). Lattice parameters of *c* of these samples were determined from the 002 diffraction line. Those of Samples UPW, NC, 0.1CC, and 1CC were 0.6879, 0.6869, 0.6852 and 0.6842 nm, respectively, while those of HA and chlorapatite are 0.6884 and 0.6771, respectively.

Figure 2 shows SEM photographs of the samples before and after the hydrothermal treatment of the samples in ultrapure water, NaCl, and CaCl₂ solutions. The samples before the treatment had interconnecting pores with a diameter of about 10 μ m. Porous ceramics consisting of rod-shaped particles with a length of about 10–50 μ m were obtained after

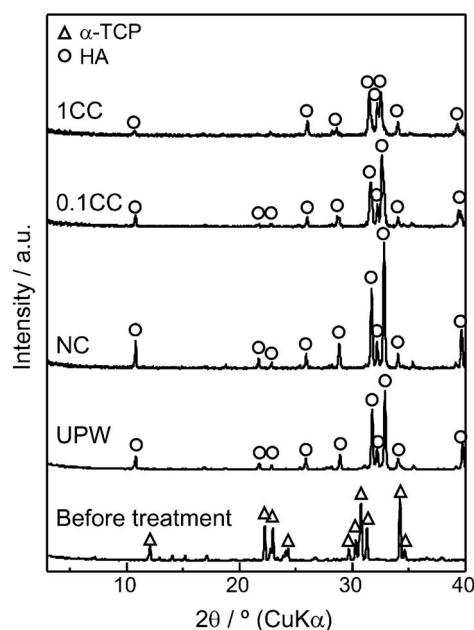


Fig. 1. XRD patterns of the samples before and after the hydrothermal treatment in ultrapure water, NaCl and CaCl₂ solutions.

the hydrothermal treatment using these solutions. From the data in Fig. 1, these rod-shaped particles were assigned to HA.

3.2 Hydrothermal treatment in Na₃PO₄, Na₂HPO₄, NaH₂PO₄, and H₃PO₄ solutions

Figure 3 shows the XRD patterns of the samples after the hydrothermal treatment in Na₃PO₄, Na₂HPO₄, NaH₂PO₄, and H₃PO₄ solutions. The phase of the samples was transformed from α -TCP to monophase HA for Samples N3P and N2HP, but the phase was transformed to biphasic HA and monetite (DCPA, CaHPO₄, PDF No. 09-0080) for Sample NH2P, and to monophase DCPA for Sample H3P.

Figure 4 shows SEM photographs of the samples after the hydrothermal treatment of the α -TCP porous ceramics in Na₃PO₄, Na₂HPO₄, NaH₂PO₄, and H₃PO₄ solutions. Needle-shaped particles with a length of about 5 μ m were observed for Samples N3P and N2HP. The inherent pore structure of the α -TCP porous ceramics was maintained in Samples N3P and N2HP. From the data in Fig. 3, these needle-shaped particles were assigned to HA. Plate-shaped particles were observed in Samples NH2P and H3P. The plate-shaped particles in Sample NH2P were assigned to HA, because from the XRD patterns, the main phase of Sample NH2P was HA, while the plate-shaped particles in Sample H3P were assigned to DCPA.

4. Discussion

When the α -TCP porous ceramics were treated with ultrapure water, the porous HA ceramics consisted of rod-shaped HA particles. It has been reported that rod-shaped HA particles are formed when α -TCP is hydrothermally treated with pure water.⁹⁾ The result in this study is consistent with that of previous work.

When an NaCl or CaCl₂ solution was used in the hydrothermal treatment, the resulting morphology was

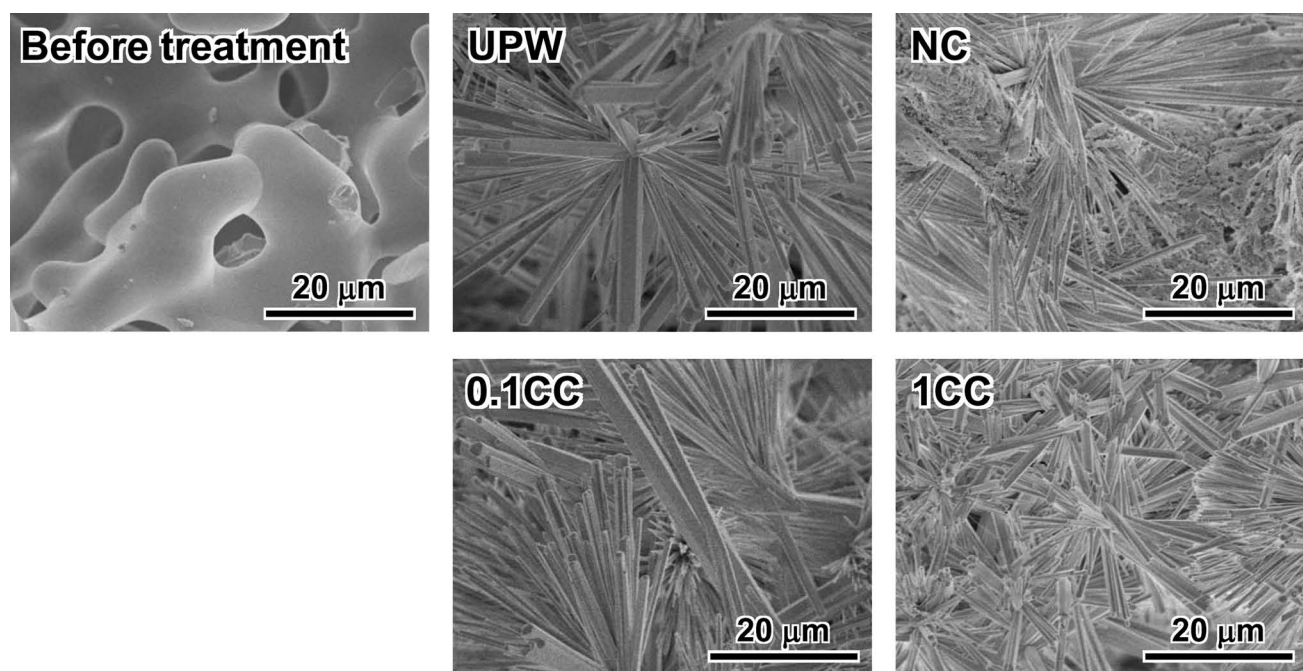


Fig. 2. SEM photographs of the samples before and after the hydrothermal treatment of the α -TCP porous ceramics in ultrapure water, NaCl and CaCl_2 solutions.

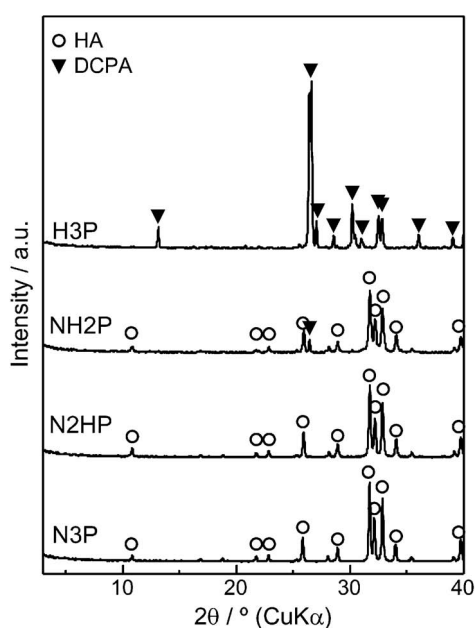


Fig. 3. XRD patterns of the samples after the hydrothermal treatment in Na_3PO_4 , Na_2HPO_4 , NaH_2PO_4 and H_3PO_4 solutions.

almost same as that in samples treated with ultrapure water. However, chloride ions (Cl^-) were incorporated into the crystal structure of the HA. The amount of incorporated chloride ions was assumed to increase with increasing Cl^- ion concentration, because the peak shift increased with increasing Cl^- ion concentration. Although we expected that the supply of Ca^{2+} ions during the hydrolysis of α -TCP would be effective because the Ca/P molar ratio of α -TCP is

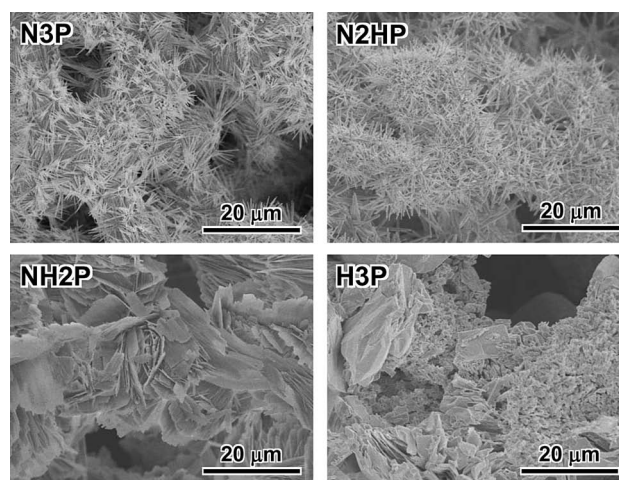


Fig. 4. SEM photographs of the samples after the hydrothermal treatment of the α -TCP porous ceramics in Na_3PO_4 , Na_2HPO_4 , NaH_2PO_4 and H_3PO_4 solutions.

1.50 and the value of Ca/P was smaller than that of stoichiometric HA ($\text{Ca/P} = 1.67$), the Ca^{2+} ions supplied by CaCl_2 did not significantly affect the morphology.

The phase in Samples N3P and N2HP was HA. These samples had smaller particles than Samples UPW, NC, 0.1CC, and 1CC. This may be due to the effect of the phosphate ions or the basic conditions in these solutions because the initial pHs of $0.1 \text{ mol} \cdot \text{dm}^{-3}$ Na_3PO_4 and Na_2HPO_4 were 12.5 and 9.4, respectively. These factors should have inhibited the crystal growth of HA, because the crystallite size was small for these solutions. DCPA was detected in Samples NH2P and H3P. DCPA is more stable

in acidic conditions than HA is.¹⁵⁾ The initial pHs of 0.1 mol·dm⁻³ NaH₂PO₄ and H₃PO₄ were 4.7 and 1.8, respectively. Therefore, the differences from Sample UPW would be due to the acidic conditions in these solutions. We speculate that DCPA forms first, and then transforms into HA in Sample NH2P, because Sample NH2P had plate-shape particles, which were similar to the DCPA in Sample H3P. Kasahara et al.¹⁶⁾ reported that HA was formed through the DCPA in acidic condition by hydrothermal process from a calcium phosphate slurry. The present consideration is supported by their report. From XRD patterns, we confirmed that most of the DCPA was transformed into HA.

The inherent pore structure of the α -TCP porous ceramics was maintained in Samples N3P and N2HP, because the HA particles were smaller than the pore size of the inherent α -TCP porous ceramics. On the other hand, inherent pore structure of the α -TCP porous ceramics was not maintained in Samples UPW, NC, 0.1CC, and 1CC, because the HA particles were larger than the pore size of the inherent α -TCP porous ceramics. Sample NH2P consisted of HA porous ceramics with plate-shaped HA particles that maintained the inherent pore structure of the α -TCP porous ceramic.

5. Summary

HA porous ceramics consisting of particles with different morphologies and sizes can be obtained using a hydrothermal treatment employing different solutions. This technique is useful to fabricate the novel HA scaffold for bone regeneration.

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