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Synthesis of morphologically controlled hydroxyapatite from fish bone by urea-assisted hydrothermal treatment and its Sr^{2+} sorption capacity

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ABSTRACT

Needle- and sponge-shaped hydroxyapatite (HAp) particles were synthesized from calcined tuna fish bone (Tn1000) and commercially available HAp reagent (ChemHAP) by a urea-assisted hydrothermal treatment using 0.1–1.0 M urea solution at 160 °C for 3 h. The Sr^{2+} sorption capacity of the synthesized HAp was also investigated using 0–50 mM Sr^{2+} solution at 25 °C for 72 h to evaluate its performance as a sorbent for environmental remediation. Sponge-shaped HAp was formed under hydrothermal conditions with a urea concentration of 1.0 M. With decreasing urea concentration, the morphology of HAp changed from sponge-shaped to needle-shaped crystals, regardless of the starting material. Some calcium carbonate and/or β-tricalcium phosphate impurities were formed from Tn1000 at 0.1–0.5 M urea concentration. The Sr^{2+} sorption mechanism of the synthesized HAp was estimated using Ca ion-exchange reaction and precipitation of $SrCO_3$. The sponge-shaped HAp crystals, which had high specific surface area and CO_3^{2-} content, exhibited a large ion-exchange capacity with Sr^{2+}. In contrast, the ion-exchange ratio of needle-shaped HAp dramatically decreased with increasing initial Sr concentration. No clear difference in Sr^{2+} sorption behaviour caused by the choice of HAp synthesis starting material was observed. These results indicate that the Sr sorption mechanism of HAp is influenced by not only its composition but also its crystal morphology.

1. Introduction

Hydroxyapatite (HAp; $Ca_{10}(PO_4)_6(OH)_2$), which is one of the calcium orthophosphates, has unique properties including ion-exchange ability, adsorptive properties, and low solubility. These characteristics of HAp make it extremely useful as a water purification material for heavy metals and radionuclides. Hence, many studies on the properties of HAp used as a sorbent have been reported over the years [1–12]. These reports show that HAp is useful for remediation of contaminants such as Pb^{2+} [1–4], Cd^{2+} [1,3–5], AsO_4^{3-} [6,7], Sr^{2+} [3,4,8], and UO_2^{2+} [8,9]. We have previously investigated the Sr^{2+} sorption capacity of HAp obtained from calcined fish bones with a focus on the lattice strain, crystallinity, and composition of the fish bones, owing to the higher crystallinity, lower Mg content, and higher Ca/P atomic ratio obtained [10–12]. In our work, calcined fish bones were found to show a Sr^{2+} sorption capacity and ion-exchange rate higher than those of chemically synthesized pure HAp [10,12]. However, HAp is a hexagonal crystal with a positively charged *a* face and a negatively charged *c* face [13]. This characteristic is considered to be dependent on exposed ionic species on the surface of HAp in water. For instance, the effects of different HAp crystal faces on adsorption behaviour have been widely discussed in studies of protein adsorption on HAp [13,14]. It is believed that this effect is also seen during reactions between target ions and water remediation materials. Generally, calcined HAp products show random crystal faces with small crystallite sizes. Therefore, it is supposed that it is difficult to observe the effect of the crystal face on the sorption of ionic species for samples prepared by calcination.

HAp with typical morphology can be easily prepared by wet chemical methods such as co-precipitation [15,16], gel growth [17], and hydrothermal synthesis [18–22]. Hydrothermal synthesis is a way of fabricating crystals with unique and well-crystallized features in a relatively short period of time at low temperature, compared with traditional methods such as molten salt synthesis, which require high temperatures [23]. Many reports show that the nature of hydrothermally synthesized HAp particles dramatically changes according to the starting material and treatment conditions, such as the use of surfactants or different solvents [18–22]. Hence, hydrothermal methods are considered to be a useful process for reforming naturally derived HAp to control its crystal morphology. However, in comparison with the synthesis by calcination process [10–12,24–26], few studies on the synthesis of morphological control or recrystallization of naturally derived HAp from animal bones using hydrothermal processes [4] have been reported.

In the present study, the hydrothermal synthesis of naturally derived HAp particles with typical morphologies was attempted by a homogeneous precipitation method using urea solution and calcined fish bone. The effects of the urea concentration and starting material

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on the crystal phase (and by-products), morphology, and the composition of the HAp products were investigated by physicochemical methods. HAp obtained from calcined fish bones was compared with chemically synthesized HAp. The relationship between the crystal morphology and Sr^{2+} sorption capacity of hydrothermally synthesized HAp is discussed.

2. Material and methods

2.1. Hydrothermal synthesis of HAp

Chemically produced hydroxyapatite (ChemHAP) (HAP-100, Taihei Chemical Industrial Co., Ltd., Osaka, Japan) and tuna bone (Tn) calcined at 1000 °C (Tn1000) were used as starting materials. The calcination of Tn has been described in detail in previous reports [11,12]. Tn1000 consists of B-type carbonated HAp and a small amount of CaO. The particle of Tn1000 shows short rods of less than 1 μm.

The starting materials were hydrothermally treated with a urea solution of different concentrations. ChemHAP or Tn1000 (0.4 g) was added to 0.1, 0.25, 0.5, and 1.0 mol/L (M) urea solutions ($(NH_2)_2CO$, Wako Pure Chemical Industries, Ltd., Osaka, Japan). Hereafter, sample names are denoted, for example, by "HAP-1 M", which indicates ChemHAP treated with 1.0 M urea solution. The mixture was stirred and its pH was adjusted to 3.5–1.5 using 6.5 M nitric acid (HNO_3, Wako Pure Chemical Industries, Ltd., Osaka, Japan). After the samples were completely dissolved, the solutions were poured into a polytetrafluoroethylene (PTFE) vessel (SAN-AI Kagaku Co. Ltd., Nagoya, Japan). The sealed vessel was then hydrothermally treated at 160 °C for 3 h, after preheating in an oven at 160 °C for 30 min. After hydrothermal treatment, the vessels were cooled to room temperature immediately and the solid products were removed by suction filtration. The products were then suspended in ultra-pure water, and the sample powders were obtained by freeze-drying to prevent aggregation.

2.2. Sorption experiments

Aqueous Sr^{2+} solutions of 0–50 mM were prepared using strontium nitrate ($Sr(NO_3)_2$, Wako Pure Chemical Industries, Ltd., Osaka, Japan). The pH of the solutions was adjusted to 10 ± 0.3 using 28% aqueous ammonia (NH_4OH, Wako Pure Chemical Industries, Ltd., Osaka, Japan). Hydrothermally synthesized sorbents (0.04 g) were placed into a 60 cm^3 plastic bottles, and 20 cm^3 of the selected aqueous $Sr(NO_3)_2$ solutions were added. The bottles were then shaken at a constant speed of 100 rpm in a mechanical shaker (BIO SHAKER; Takasaki Scientific, Ins., Corp., Saitama, Japan) at 25 °C for 72 h. After the sorption experiment, the sorbent and solution were separated by filtration, and the sorbents were dried at 40 °C.

2.3. Characterisation

The crystalline phases of the prepared samples were identified by X-ray diffraction (XRD; Ultima IV, Rigaku Co., Tokyo, Japan) using CuKα radiation at 40 kV and 40 mA. The crystal morphology of the samples was observed using scanning electron microscopy (VE-9800, Keyence Corp., Osaka, Japan) at an acceleration voltage of 20 kV, and transmission electron microscopy (TEM; JEM-2010HCKM, JEOL Ltd., Tokyo, Japan) at 200 kV. Electron diffraction patterns were also collected by TEM (JEM-2000EX, JEOL Ltd., Tokyo, Japan). The functional groups present in the products were characterized using Fourier transform infrared spectrometry (FT-IR; FT/IR-670plus, JASCO Co., Tokyo, Japan) in transmission mode using potassium bromide. The specific surface areas (SSA) of the products were determined by a single point BET method (BELSORP-MR6, BEL Japan, Inc., Osaka, Japan). The elemental composition of the products was determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Optima 8300, PerkinElmer Japan Co., Ltd., Yokohama, Japan). The samples for ICP-OES analysis were decomposed in 6.5 M HNO_3 and diluted to various concentrations. ICP-OES analysis was measured once or twice for samples, respectively. The amount of C, H, and N elements in the products were determined by CHN analysis (CHN Corder MT-5, Yanaco Technical Science Co., Ltd., Tokyo, Japan). Extended X-ray adsorption fine structure (EXAFS) spectra of the Ca K-edge were measured using an ionization chamber in transmission mode on the Kyushu University Beamline (BL-06) of Kyushu Synchrotron Light Research Centre (SAGA-LS; Tosu, Japan). Pellet samples for EXAFS measurement were prepared as mixtures with boron nitride. Ca K-edge EXAFS spectra were collected over a photon energy range of 3.7–5.6 keV. The collected spectra were analysed using REX 2000 software (Rigaku Co., Tokyo, Japan). HAp (HAP-200, Taihei Chemical Industrial Co., Ltd., Osaka, Japan), β-tricalcium phosphate (β-TCP; $Ca_3(PO_4)_2$, Taihei Chemical Industrial Co., Ltd., Osaka, Japan), and calcium carbonate ($CaCO_3$, Wako Pure Chemical Industries, Ltd., Osaka, Japan) were used as reference samples for EXAFS analysis.

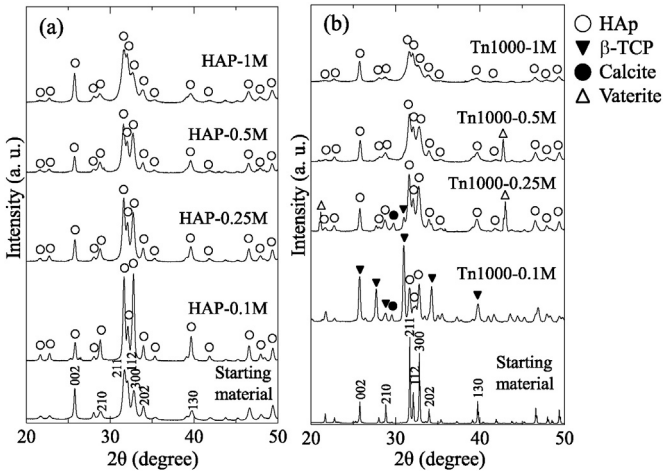

Fig. 1. X-ray diffraction patterns of samples before and after urea-assisted hydrothermal treatment of (a) ChemHAP and (b) Tn1000 for 3 h at 160 °C.

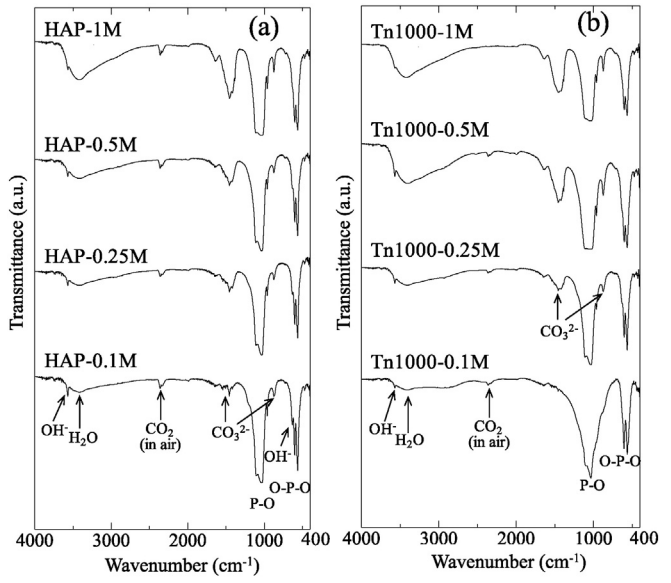

Fig. 2. Fourier transform infrared spectrometry spectra of the products obtained after hydrothermal treatment of (a) ChemHAP and (b) Tn1000 using 0.1–1 M aqueous urea solution.