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Preparation and characterization of thermally stable nanohydroxyapatite

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Rod-like hydroxyapatite was synthesized by precipitating calcium nitrate tetrahydrate and ammonium dibase phosphate in the presence of polyacrylic acid followed by hydrothermal treatment. Both polyacrylic acid and the hydrothermal treatment stabilised the hydroxyapatite.

1. Introduction

Biological composites, such as bone and teeth, contain hydroxyapatite (HAp), a mineral component with composition $Ca_{10}(PO_4)_6(OH)_2$. The hydroxyapatite crystallizes into hexagonal rhombic prisms and has unit cell dimensions $a = 0.9432$ nm and $c = 0.6881$ nm [1]. Polycrystalline hydroxyapatite has a high elastic modulus (40–117 GPa). The ideal Ca/P ratio of hydroxyapatite is 10:6 and the calculated density is 3.219 g/cm^3. Electron micrographs show that the HAp of bone has a platelet shape with a very small size, about (1.5–3.5 nm) × (5.0–10.0 nm) × (40.0–50.0 nm) [2].

Hydroxyapatite (HAp) has been synthesized and used for manufacturing various forms of implants [1]. Plasma-sprayed coatings of HAp on titanium prostheses is one important development for implants. During the plasma-sprayed coating, the HAp powder is exposed to very high temperature in the plasma gun [3]. Additionally, the fracture strength of HAp can be increased by increasing the sintering time and temperature [4]. In order to prevent HAp powders from decomposing to tricalcium phosphate (TCP) at temperatures above 900 °C [1, 5], the development of thermally stable, pure HAp has become a significant issue for implant applications.

In this paper, we provide a new method of preparing thermally stable, rod-like HAp. Most synthetic hydroxyapatite is made by adding a solution of ammonium dibase phosphate to a solution of calcium nitrate tetrahydrate at 70 °C at pH = 8.0–9.5 [6]. Another method for synthesizing hydroxyapatite is by the addition of an aqueous solution of phosphoric acid to aqueous calcium hydroxide [7]. Spherical powders of hydroxyapatite have been prepared by the sol–gel process [8]. Hydroxyapatite whiskers are usually prepared by hydrothermal treatment [9–11]. In our previous work [12, 13], polyacrylic acid was used as an additive to modify chitosan-film surfaces to promote calcium carbonate crystal growth on the film surface. Pure and thermally stable HAp was obtained by adding low molecular weight polyacrylic acid into calcium nitrate and ammonium dibase phosphate, followed by hydrothermal treatment.

2. Experimental procedures

The solution (30 ml) was prepared by dissolving 7.63 g calcium nitrate tetrahydrate in deionized, distilled water free of carbon dioxide under nitrogen in a three-neck flask. The pH of the solution was adjusted to 10 using ammonium hydroxide. Low molecular weight (MW 2000) polyacrylic acid (2.0 g) was added to the solution. After dissolving the polyacrylic acid the pH of the solution was adjusted to 10 and a gel was formed. The solution was then heated to 70 °C. A 30 ml solution of 2.55 g ammonium dibase phosphate, pH = 10, adjusted by ammonium hydroxide, was then dropped into the above calcium nitrate solution. The molar ratio of calcium to phosphorous Ca/P was 1.67. The reaction proceeded at 90 °C overnight. The starting precipitate was centrifuged at 10 000 ppm for 15 min and washed with deionized and distilled water twice. The starting precipitates without polyacrylic acid were prepared in a similar way to that described above. Both starting precipitates were treated hydrothermally in a small bomb at 130 °C for 6 h. The products were dried in a vacuum oven at 100 °C overnight. The products were sintered in a large furnace at a rate of 30 °C/min to 1100 °C and kept at this temperature for 2 h, or were calcined in a thermogravimetric analyser (TGA) at a rate of 10 °C/min to 1100 °C and kept at this temperature for 2 h.

The morphology of the starting precipitates and the sintered products was observed by transmission electron microscopy (TEM, Phillips EM300). The crystal structure was measured by X-ray diffraction (XRD, Norelco X-ray diffraction unit with wide range gonimeter) and the ratio of calcium to phosphorous of powder surface was determined by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer, 5300) suing AlK_α source (600 W, 15 keV) with pass energy 37.5 eV. The transmission infrared spectra were obtained

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TABLE I Sample preparation conditions

	Starting precipitates	Hydrothermal treatment (130 °C)	Calcined (1100 °C)	Hydrothermal treatment and sintered at 1100 °C
Without PAA	P-1	H-1	S-1	SH-1
With PAA	P-2	H-2	S-2	SH-2

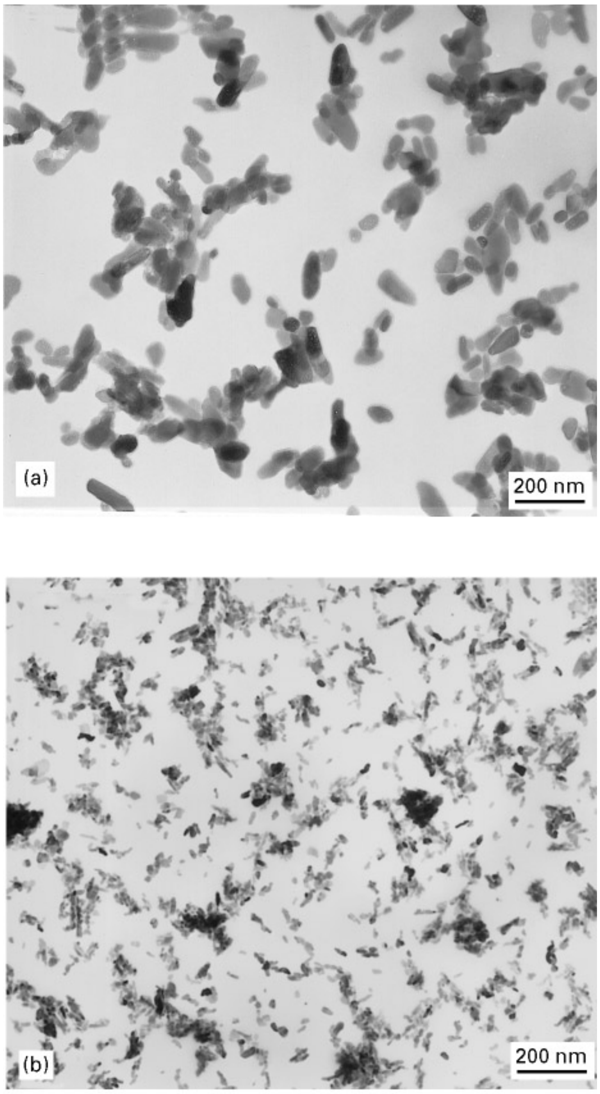

Figure 1 TEM photographs of rod-like crystals of HAp after hydrothermal treatment: (a) without polyacrylic acid (H-1); (b) with polyacrylic acid in the system (H-2).

by the KBr method using a Fourier transform infrared spectrometer (Nicolet 60SX). Simultaneous thermogravimetry and differential thermal analyses (TG-DTA, Netzsch, STA 409) were performed using a thermoanalysis apparatus in air at a heating rate of 10 °C/min.

3. Results and discussion

Table I shows the sample preparation conditions. Here, 1 represents the system without polyacrylic acid and 2 the system with polyacrylic acid in the starting precipitates.

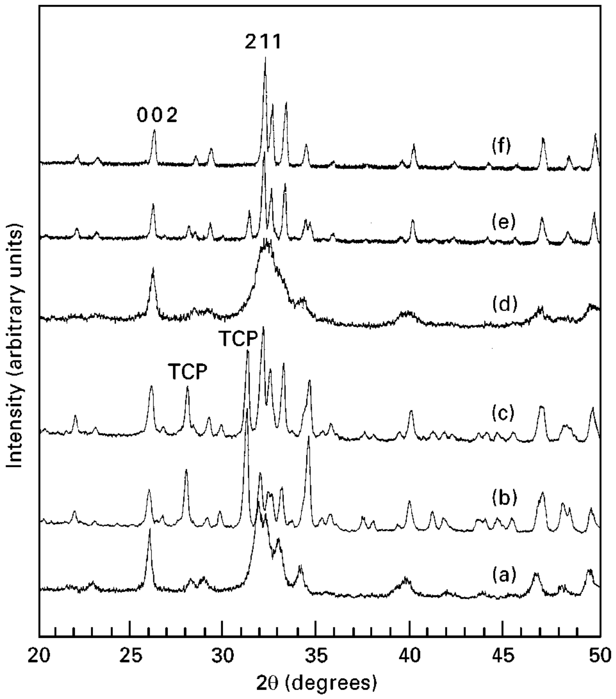

Figure 2 XRD patterns of the starting precipitates and the hydrothermal treatment before and after sintering at 1100 °C: (a) P-1; (b) S-1; (c) SH-1; (d) P-2; (e) S-2; (f) SH-2.

Typical TEM micrographs of de-agglomerated hydrothermally treated hydroxyapatite nanoparticles are shown in Fig. 1. Fig. 1a is for sample H-1 and Fig. 1b pertains to H-2. Rod-like particles were obtained by hydrothermal treatment. The whiskers without PAA and with PAA are of length 50 nm and 25 nm, respectively. In the presence of polyacrylic acid, the particle size was reduced.

Fig. 2 shows XRD patterns of starting precipitates (Fig. 2a, 2b) and the products (Fig. 2c, 2d, 2e) after calcining at 1100 °C for 2 h. Curve 2a is that for starting precipitates without polyacrylic acid in the system (P-1), and curve 2c is for the same precipitates fired at 1100 °C for 2 h (S-1); trace 2b is for starting precipitates with polyacrylic acid in the system (P-2), and curve 2d is for the same precipitates fired at 1100 °C for 2 h (S-2). Curve 2e is for a sample subjected to hydrothermal treatment and then calcined at 1100 °C for 2 h. The starting precipitates, both with and without polyacrylic acid, have poorly crystallized apatite structure. Only the (0 0 2) plane of HAp at $2\theta = 25.6°$ is shown in the patterns. A broad peak at 2θ (30.5°–33°) is obtained in both systems. After calcining the starting precipitates at 1100 °C for 2 h, the difference in XRD patterns between the two systems is obvious. A pure HAp well-crystallized structure (Fig. 2e, SH-2) is obtained from the system containing

TABLE II Effects of different preparation conditions on properties of products

Sample	Average crystal grain size (nm)	Ca/P ratio of HAp powder surfaces	Crystallinity	The relative ratio of HAp/TCP by XRD patterns
P-1	11.4	1.66	low	
H-1	11.4		medium	
S-1	24	1.50	high	0.3/0.7
SH-1	24		high	0.6/0.4
P-2	11.4	1.73	low	
H-2	11.4		low	
S-2	24	1.66	high	0.9/.01
SH-2	24		high	1.00/0

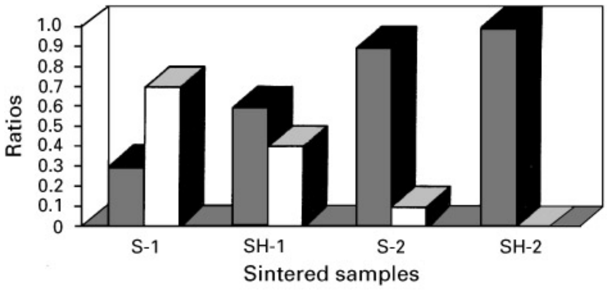

Figure 3 The relative ratio of HAp (■) to TCP (□), determined by the peak intensity ratio of a HAp peak at $2\theta = 25.9°$ and a TCP peak at $2\theta = 31.5°$.

polyacrylic acid and treated hydrothermally. A well-crystallized structure is also observed in the sample S-2, however, it is a mixture of TCP (tricalcium phosphate) and HAp (Fig. 2d, S-2). Therefore, hydrothermal treatment and polyacrylic acid addition stabilized the synthetic hydroxyapatite.

The average grain size can be estimated by the Sherrer formula [14], assuming particles are spherical and stress free:

$$t = 0.9\lambda / B \cos\theta$$

Here λ is the wavelength of the X-rays (0.1542 nm) (CuK_α) for the present experiment, θ is the diffraction angle, and B (in radians) is the measured width at the half height of the diffraction peak. Here the (0 0 2) plane peak was used with $2\theta = 25.9°$. The results are listed in Table II. The relative ratios of HAp to TCP were determined by comparing the intesities of the peak at $2\theta = 25.9°$, which represents the HAp, and the peak at $2\theta = 31.5°$, which represents the TCP phase. The results are listed in Table II and Fig. 3. The relative ratio of HAp/TCP decreases as the preparation conditions change from S-1 to SH-2.

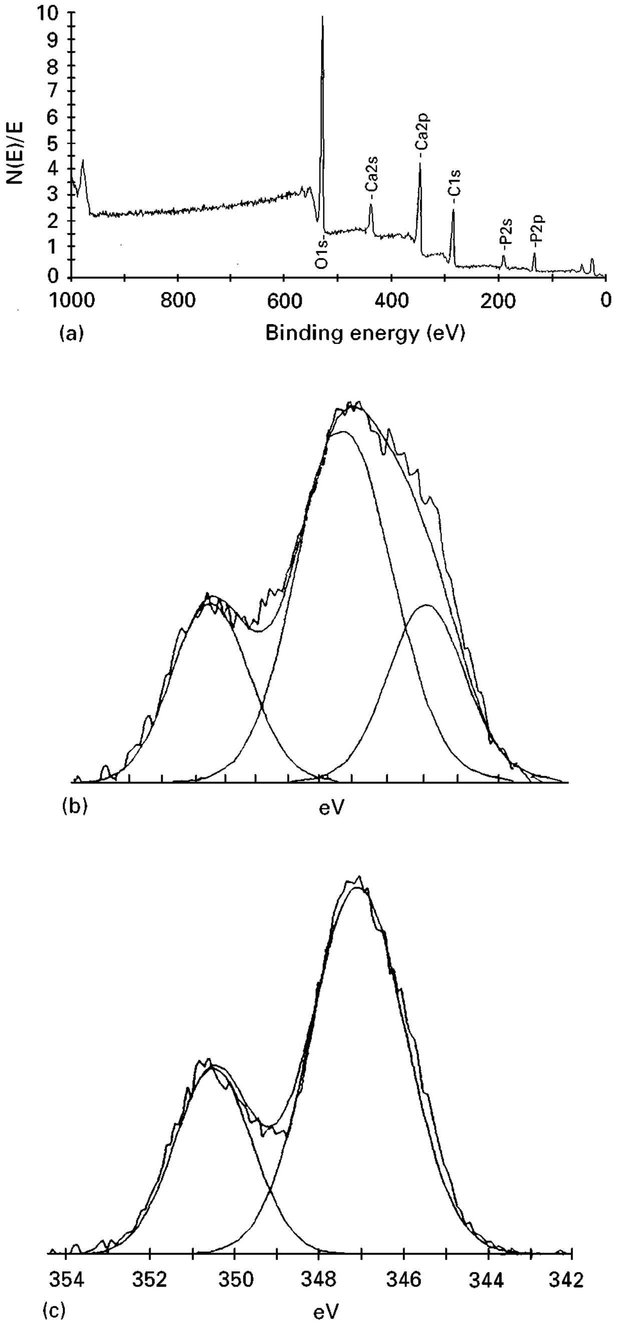

Figure 4 XPS wide scan (a) core spectra of HAp powder surface: (b) P-2; (c) S-2.

XPS was used to determine the ratio of Ca/P at the powder surfaces. Fig. 4a shows the XPS wide scan and core spectra of elemental calcium for the system with polyacrylic acid. Fig. 4b shows the spectrum of the calcined sample and Fig. 4c shows the spectrum of the starting precipitate. Nitrogen did not appear in the wide scan spectrum of the starting precipitate with polyacrylic acid, which indicates absence of ammonium ions or nitrate ions on the hydroxyapatite powder surface. Fig. 4a is a typical XPS core spectrum for Ca2p which has two peaks separated by 3.5 eV in bonding energy. Another calcium peak appeared at low binding energy, with area approximately 20% of the total calcium element, which matches the amount

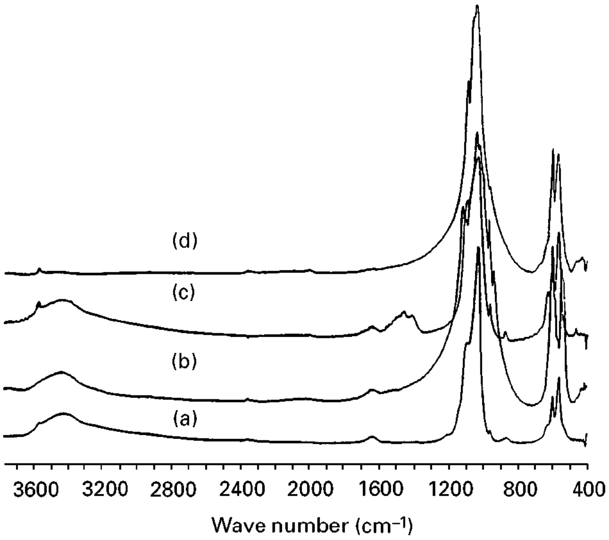

Figure 5 IR spectra of the starting precipitates and crystals sintered at 1100 °C: (a) P-1; (b) S-1; (c) P-2; (d) SH-2.

of PAA added. This calcium is bonded to polyacrylic acid [13, 14]. A weight loss of 20% also appeared in the TGA curve in the temperature range 300–400 °C. The detailed mechanisms of how the polyacrylic acid stabilizes the hydroxyapatite during calcining up to 1100 °C is under further investigation.

The FTIR spectrum in Fig. 5 indicates the presence of OH^-, HPO_4^{2-}, PO_4^{3-} in the starting precipitates and the sintered products. The characteristic peaks in hydroxyapatite, corresponding to PO_4^{3-} (560–600 cm^{-1}, 1030–1090 cm^{-1}) are shown in all the spectra. The 1033 and 963 cm^{-1} bands are assigned to the stretching vibrations of PO_4^{3-} ions, and the 604 and 564 cm^{-1} bands are assigned to the deformation vibrations of PO_4^{3-} ions. The 1102 and 875 cm^{-1} bands are due to the P–O stretching vibrations and deformation of P–OH groups of HPO_4^{2-} ions. The band due to the stretching vibrations of OH^- ions appears at 3574 cm^{-1}, and the 635 cm^{-1} band is due to the vibration motion of the OH^- ions [10]. In system 1, two shoulders at 3570 cm^{-1} and 635 cm^{-1} appear, however, the two shoulders disappear after calcining at 1100 °C for 2 h. Combining the XRD pattern with the TG-DTA thermogram, it appears that poorly crystallized HAp changes to TCP after firing (S-1). For system 2, on the other hand, the two bands representing OH^- ions appear in the spectrum of the starting precipitate. The small band occurring at 1635 cm^{-1} and broad band at 340 cm^{-1} correspond to hydrate in the materials. Spectrum Fig. 3d representing SH-2 does not have water peaks remaining, only the band at 3574 cm^{-1} due to OH^- ions.

4. Conclusions

To summarize, rod-like, pure hydroxyapatite can be synthesized by precipitating calcium nitrate tetrahydrate and ammonium dibase phosphate from aqueous solution in the presence of polyacrylic acid followed by hydrothermal treatment. Both PAA and hydrothermal treatment stabilize the hydroxyapatite.

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