



Controlled growth of hydroxyapatite fibers precipitated by propionamide through hydrothermal synthesis

Lijing Hao, Hui Yang, Naru Zhao, Chang Du, Yingjun Wang*

School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China
National Engineering Research Center for Tissue Restoration and Reconstruction, Guangzhou 510006, China
Guangdong Province Key Laboratory of Biomedical Engineering, South China University of Technology, Guangzhou 510006, China

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ABSTRACT

Hydroxyapatite fiber (fHA) was hydrothermally synthesized using propionamide (PA) as a pH adjusting agent. The concentrations of PA and calcium ion (Ca), as well as synthetic temperature and time, were regulated and investigated in detail to explore the formation mechanism of fHA. The results demonstrated that the morphology of fHA was susceptible to the concentrations of PA and Ca, while the composition and crystallinity were not. The morphology of fHA changed from long fibers to flowers and thorn-like bundles with increasing concentrations of PA and Ca, respectively. Higher temperature was shown to contribute to the generation of highly crystalline fHA. By further combining the theories of oriented attachment and Ostwald ripening with spiral growth mechanism, it was proposed that dicalcium phosphate (DCPA) sheets were first formed via the self-assembly of nanoplatelets derived from nucleation. The sheets were then converted into the final fHA through spiral growth.

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1. Introduction

Hydroxyapatite (HA) is one of the most extensively studied calcium phosphates and has been widely used in a variety of applications, such as biomaterials, ion exchangers, adsorbents and catalysts [1,2]. It is widely used in bone repair due to its chemical similarity to human bone. However, HA is not qualified for load-bearing situations due to its poor flexural strength and fracture toughness. This limits its further application in hard tissue regeneration [3]. Therefore, the development of HA with improved reliability is badly demanded. Fibers generally exhibit high tensile properties because of their low dislocation density [4]. Hence, HA fiber (fHA) has attracted considerable attention in its application as a reinforcing component in biomedical composite materials.

fHA can be produced by diverse methods such as wet chemical precipitation [5], solid-state reaction [6], hydrolysis [7] and hydrothermal synthesis [8]. Compared with other methods, the hydrothermal method has been proven to be a convenient way to obtain fHA powders with advantages such as high crystallinity, good dispersibility, high purity and a defect-free crystal. In hydrothermal synthesis, a pH adjusting agent is often used to control the pH value of the reaction solution. So far, urea, formamide and acetamide are commonly used pH adjusting agents to prepare fHA hydrothermally [9]. However, fHA derived from urea and formamide has carbonate contamination and unsatisfying low aspect ratio. Although long and uniform fHA with high aspect ratio

can be prepared using acetamide [10], the mechanism of crystal growth is still unclear.

Propionamide is hydrolyzed to change the pH value of the synthesis solution with the increase of hydrothermal temperature. The pH changes might change in supersaturation degree of the calcium and phosphate solution, affecting the formation and growth of HA. In this work, fHA with uniform morphology was hydrothermally synthesized using PA to control the pH. The effects of processing parameters on nucleation and growth were studied in detail to elucidate the formation mechanism. Particularly, the crystalline behavior along with the reaction time was monitored to reveal the growth of fHA.

2. Material and methods

2.1. Materials

The starting materials used in this study included calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, AR, Guangzhou Chemical Reagent Factory, China), ammonium phosphate ($(\text{NH}_4)_2\text{HPO}_4$, AR, Guangzhou Chemical Reagent Factory, China), propanamide ($\text{C}_3\text{H}_7\text{NO}$, 96%, Aladdin Chemical Reagent Company, China), nitric acid (HNO_3 , AR, Guangzhou Chemical Reagent Factory, China), and ammonium hydroxide (NH_4OH , AR, Shanghai Chemical Reagent Factory, China). All of the materials were used without any further purification.

2.2. Synthesis of fHA powders

First, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$ and PA were dissolved respectively in a 0.5 M HNO_3 solution. The Ca/P molar ratios of all samples

* Corresponding author at: School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China. Tel.: +86 20 87112160; fax: +86 20 22236088.

E-mail address: imwangyj@163.com (Y. Wang).

were fixed at 1.67. Then, the initial pH was adjusted to 3 using 2 M HNO₃ or 1:1 (v/v) ammonia. The adjusted solutions were immediately transferred to teflon-lined stainless steel autoclave and sealed. The autoclave was maintained at the predetermined temperature for different times and then allowed to cool naturally. The products were then collected, washed five times with distilled water and dried at 80 °C overnight. Table 1 listed the detailed reaction conditions of each sample. The concentrations of PA and Ca, hydrothermal reaction temperature and time were the main factors investigated.

2.3. Characterization

The phase compositions of the obtained products were characterized by X-ray diffraction (XRD) (X'Pert Pro, PANalytical B.V., Netherlands) with Cu K α radiation ($\lambda = 1.5418$ Å) at a 2θ range of 10–80°. The chemical functional groups were investigated by Fourier transform-infrared spectroscopy (FTIR) (Vector 33, Bruker, Germany) within the wavenumber range of 4000–400 cm^{−1} using KBr as the standard. The morphology of the fHA was observed by scanning electron microscopy (SEM) (Quanta 200 SEM, FEI, Netherlands) and transmission electron microscopy (TEM) (JEM-2100HR, Japan). The pH values of solutions were detected by a digital pH meter (PHS-3C, Shanghai Lei Ci Device Works, China).

3. Result

3.1. Role of the concentrations of PA and Ca

The XRD patterns of fHA samples prepared at different concentrations of PA and Ca were shown in Fig. 1. The diffraction peaks in each pattern can be well indexed to the phase of HA (JCPDS card no. 72-1243) and no peaks from any impurity were identified. The sharp peaks revealed that fHA products were highly crystalline. However, the strongest peak intensity appeared at the (3 0 0) lattice plane, rather than the (2 1 1) which is as usual for HA. The reason may be that crystal grew along the c-axis, which leads to increased development of the a-plane [11,12]. The results showed that highly crystalline fHA could be easily obtained under different concentrations of PA and Ca.

The FTIR spectra of fHA prepared at different concentrations of PA and Ca were shown in Fig. 2. The absorption bands were in good agreement with the bands of HA and no obvious shift could be found. The bands at 3570 cm^{−1} (ν_s) and 634 cm^{−1} (ν_L) were assigned to OH[−] [13]. The characteristic bands originating from PO₄^{3−} appeared at 1094 cm^{−1} (ν_{3a} of P–O), 1030 cm^{−1} (ν_{3c} of P–O), 963 cm^{−1} (ν_1 of P–O), 602 cm^{−1} (ν_{4a} of O–P–O), 565 cm^{−1} (ν_{4b} of O–P–O), and 471 cm^{−1} (ν_{2a} of O–P–O) [14,15]. The broad band around

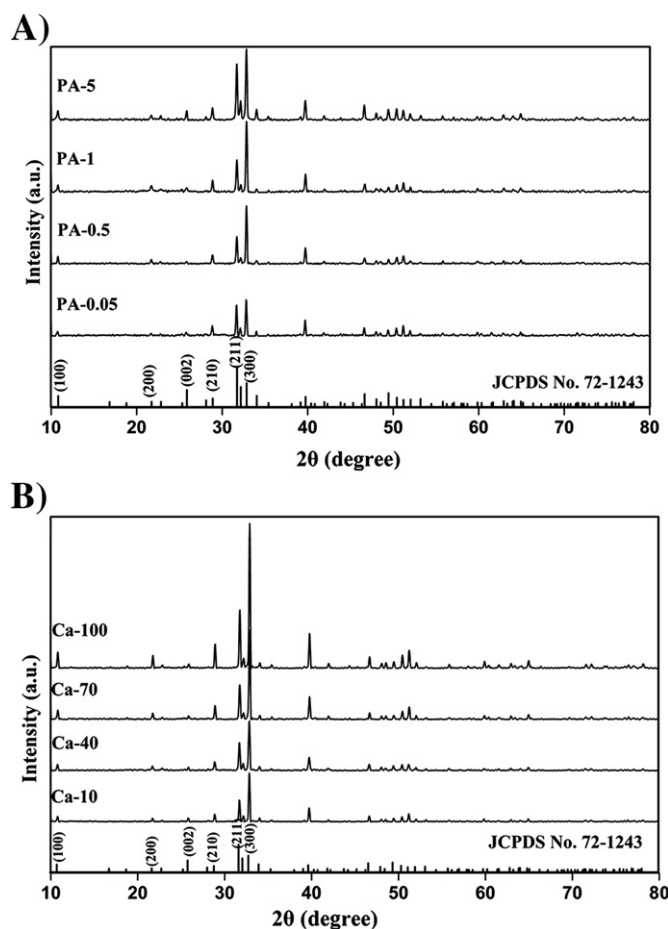


Fig. 1. XRD patterns of products prepared at 180 °C for 24 h at a fixed Ca/P ratio of 1.67 using various concentrations of PA (A) and Ca (B).

3500–3200 cm^{−1} and weak band at 1640 cm^{−1} were assigned to H₂O [16,17]. In addition, the band due to HPO₄^{2−} appeared at 868 cm^{−1} (ν_5 of P–O(H)) [18], indicating existence of calcium deficiency. The products were free of CO₃^{2−} shown by the absence of bands at 1410–1450 cm^{−1}. These demonstrated that no impurity existed in fHA except slight calcium deficiency.

The SEM images of the products obtained at different concentrations of PA and Ca were shown in Fig. 3. The products had a fibrous morphology at the PA concentration of 0.05 M (Fig. 3A). When the concentration reached 0.5 M and 1 M, the fibers became several micrometers in width and hundreds of micrometers in length (Fig. 3B,C). As the concentration of PA further increased to 5 M, the microflowers consisting of aggregated small fibers appeared (Fig. 3D). fHA broadened at low Ca concentration, forming irregular plate-like particles (Fig. 3E). As Ca concentration increased to 40 and 70 mM, the products became more uniform and tenuous (Fig. 3F,G). However, when the concentration was as high as 100 mM, the products then became into smaller fibers, which tended to aggregate into small fibrous bundles (Fig. 3H). The results from XRD, FTIR and SEM showed that the morphologies of fHA were susceptible to the initial concentrations of PA and Ca, but the crystallinity and composition were not.

3.2. Role of the synthetic temperature and time

The XRD patterns of fHA samples prepared under different reaction temperatures and periods were shown in Fig. 4. At the temperature of 90 °C (Fig. 4A), there almost no peaks, indicating that the products were amorphous. As the temperature rose, the main peaks at (100),

Table 1
The reaction conditions of hydrothermal synthesis.

Experiment	PA/(mol/L)	[Ca]/(mmol/L)	T/(°C)	t/(h)	Final pH
PA-0.05	0.05	30	180	24	3.32
PA-0.5	0.5	–	–	–	4.70
PA-1	1	–	–	–	5.25
PA-5	5	–	–	–	5.62
Ca-10	0.3	10	–	–	5.53
Ca-40	–	40	–	–	5.02
Ca-70	–	70	–	–	4.69
Ca-100	–	100	–	–	4.50
T-90	–	30	90	–	3.97
T-120	–	–	120	–	4.04
T-150	–	–	150	–	4.66
T-180	–	–	180	–	5.19
t-0.5	1	60	–	0.5	3.65
t-1	–	–	–	1	3.73
t-6	–	–	–	6	4.10
t-24	–	–	–	24	5.59

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