



# Manipulation of partially oriented hydroxyapatite building blocks to form flowerlike bundles without acid-base regulation



Zhenliang Wen<sup>a,1</sup>, Zihao Wang<sup>a,1</sup>, Jingdi Chen<sup>a,\*</sup>, Shengnan Zhong<sup>a</sup>, Yimin Hu<sup>a</sup>, Jianhua Wang<sup>a</sup>, Qiqing Zhang<sup>a,b,\*\*</sup>

<sup>a</sup> Institute of Biomedical and Pharmaceutical Technology, Fuzhou University, Fuzhou 350002, China

<sup>b</sup> Institute of Biomedical Engineering, Chinese Academy of Medical Science and Peking Union Medical College, Tianjin 300192, China

## ARTICLE INFO

### Article history:

Received 16 October 2015

Received in revised form 11 January 2016

Accepted 7 February 2016

Available online 10 February 2016

### Keywords:

Hydroxyapatite

Shape control

Surfactant

Chelating agent

Bone-like structure

## ABSTRACT

The application of hydroxyapatite (HAP) in different fields depends greatly on its morphology, composition and structure. Besides, the main inorganic building blocks of human bones and teeth are also HAP. Therefore, accurate shape and aggregation control and of hydroxyapatite particles will be of great interest. Herein, oriented bundles of flowerlike HAP nanorods were successfully prepared through hydrothermal treatment without acid-base regulation, with the mono-alkyl phosphate (MAP) and sodium citrate as surfactant and chelating agent, respectively. The prepared samples were characterized by the X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and zeta potential, the pH value and conductivity value of suspension were characterized by pH meter and conductivity measurement. The results showed that the MAP and citrate play an important role in assembly of HAP nanorods without acid-base regulation. Citrate calcium complex could decompose slowly and release citrate ions at hydrothermal conditions. Besides, the further decomposition of citrate ions could release aconitic acid as the reaction time prolongs. Moreover, the possible scheme for the formation process was discussed in detail.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , HAP) has similar chemical composition and structure with the minerals in natural bone tissues and enamel, and it can be used in bone substitute [1–6]. HAP widely used as gene transfection [7], drug carrier [8], and catalyst [9]. The performance of HAP in the above applications depends greatly on its morphology, composition and structure. In recent years, self-organization of meso-, micro-, and nanostructured building blocks has become an active research field in materials synthesis and device fabrications. HAP crystals with plate-shaped structures in natural bone and with hexagonal prisms in dentin assemble like building blocks to form the hard structure [10–12]. Therefore, the research about how to manipulate the sizes and shapes

of hydroxyapatite particles using nanocrystals as building blocks will be of great interest. A bundle formation of c-axis oriented HAP nanocrystals automatically without any physical support is regarded probably plays an important role in bone metabolism and mechanical properties [13].

Surfactants can self-assemble into rod-like micelles or lamellar structures at high concentrations so they can be used to modify the desired size and shape of HAP [14–16]. Surfactants act as organic template that regulate the nucleation and growth of HAP through electrostatic, stereo-chemical and geometric interactions. As reported, many researchers have explored many organic matters to synthesize nano/micro HAP particles with well-defined morphologies and accurate size by manipulating the building blocks of HAP crystals, this approach is also called as template method. There are many kinds of template method, including microemulsions templating method, monodisperse colloidal crystals templating method, pore-making agent method, sponges gel-casting method, etc.

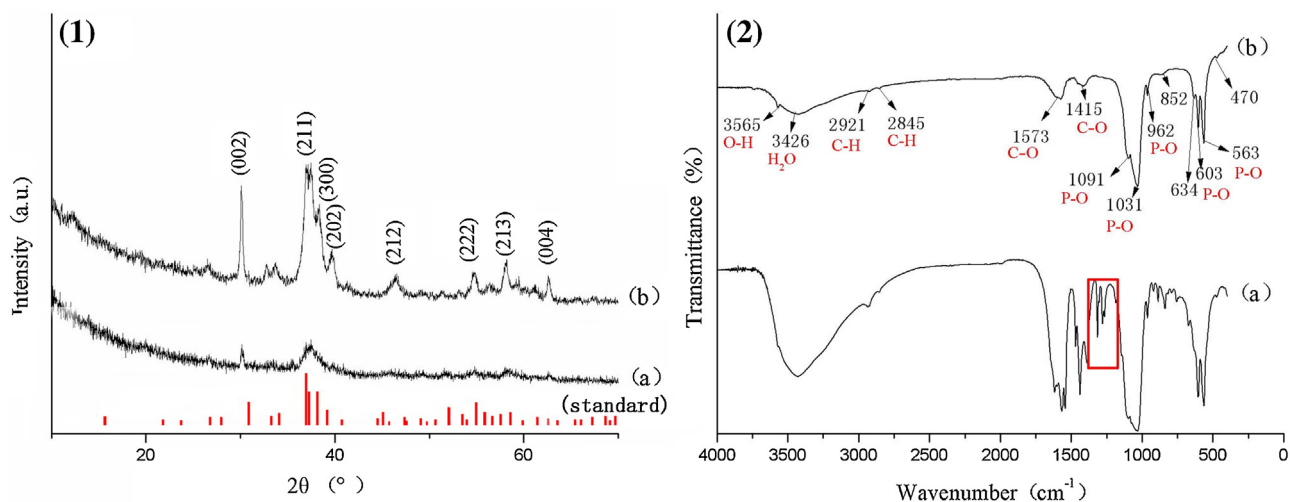
The template method could direct the shapes of HAP and realize partially oriented hydroxyapatite building block, it seems that it is difficult to form complicated structure through only template

\* Corresponding author at: Institute of Biomedical and Pharmaceutical Technology, Fuzhou University, No. 523 Gongye Road, Fuzhou 350002, China.

\*\* Corresponding author at: Institute of Biomedical Engineering, Chinese Academy of Medical Science and Peking Union Medical College, Tianjin 300192, China.

E-mail addresses: [ibptcjd@fzu.edu.cn](mailto:ibptcjd@fzu.edu.cn) (J. Chen), [zhangqiq@126.com](mailto:zhangqiq@126.com) (Q. Zhang).

<sup>1</sup> These authors contributed equally to the work.



**Fig. 1.** XRD patterns (1) and FTIR spectra (2) of (a) control without MAP and (b) sample with MAP. The samples were synthesized at hydrothermal temperature 140 °C for 24 h.

method [17]. In addition, the residue of surfactant results in poor biocompatibility which limit their application in bone tissue engineering. Furthermore, the alkaline condition for synthesis of HAP is totally different from the extracellular cartilage matrix of inner environment of human body. Hydrothermal method based on the high temperatures and pressures is a convenient preparing process but a poor control in the morphology [18–20].

Many researchers believed that the relationship between citrate and calcium phosphate mineralization is complex and become the research subject for many scientist, they found that citrate could drive the conversion of brushite to more stable HAP and could affect the size and morphology of HAP as well [21–23]. The combination of organic matrix (template) and hydrothermal method seems a promising way to enable the manipulation of the building blocks of HAP crystals and obtain interesting structure of HAP with citrate as a calcium ions chelating agent. Furthermore, partially oriented HAP bundles with complicated structure could be obtained, the realization of bone-like microstructure manipulation will not be far.

We aimed to investigate the relationship between organic template and inorganic crystal and further to interpret the crystal growth mechanism. Therefore, we perform a new combination of surfactant (mono-alkyl phosphate, MAP) and citrate to prepare flowerlike bundles hydroxyapatite by hydrothermal treatment without acid-base regulation. The morphology and size of the samples could be modified by sodium citrate as chelating agent and MAP as surfactant, respectively. The possible mechanism of the morphogenesis of the structure and interaction between organic and inorganic phase was investigated. The regulation of single HAP crystal in flowerlike bundles will be helpful to understand the biomimetic mineralization process and realize the bone-like microstructure manipulation.

## 2. Experimental

### 2.1. Materials

**Materials and method:** In this study, analytical grade Calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) and Ammonium hydrogen phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ) were used as calcium and phosphorus sources. Sodium citrate was used as chelating agent. Absolute ethylalcohol (AR) and distilled water were used as solvent. These reagents above were purchased from Sinopharm Chemical Reagent

Co., Ltd. MAP (Wuxi Ideal Chemical Co., Ltd, china) was used as template.

### 2.2. Methods

A typical experiment as follows: A solution of Calcium nitrate tetrahydrate and Sodium citrate (molar ratio of Calcium nitrate tetrahydrate to Sodium citrate 1:1, 45 ml) was vigorously stirred for 12 h at room temperature; 30 ml distilled water and 30 ml absolute ethyl alcohol was added to 1.5 g MAP and 0.48 g Ammonium hydrogen phosphate stirred at room temperature for 15 min. Then the solution was added dropwise into the former solution under vigorous stirred with the aid of a magnetic stirrer. After vigorous agitation for 25 min, the mixture suspension was characterized by pH meter and conductivity meter and then put in a Teflon-lined stainless steel autoclave and aged at 140 °C in an oven. The following steps are the same as those for the synthesis under different hydrothermal temperature. Finally, a series of samples was produced and named 3 h, 6 h, 12 h, 24 h and 48 h. After cooling down with the room temperature, the original precipitate was washed, ultracentrifugated (4000 rpm) and freeze dried at  $-110$  °C for 2 days. After that, the samples were obtained. A control product was prepared by the same procedures but without the addition of MAP.

### 2.3. Characterization

#### 2.3.1. X-ray diffraction analysis (XRD)

The phase of samples were examined using X-ray diffraction (XRD) (Philips X'Pert MPD Pro) with monochromatized  $\text{Co K}\alpha$  radiation ( $\lambda = 0.178$  nm) at a working voltage of 40 keV in a  $0.02^\circ$  step size, in the range from  $10^\circ$  to  $70^\circ$ . The phases were identified by comparing the data with data reported in the Joint Committee of Powder Diffraction Standards database (JCPDS No. 09–0432).

#### 2.3.2. Fourier transform infrared spectroscopy (FTIR)

Functional group identification of the sample was obtained using Fourier transform infrared spectroscopy (FTIR) (Nicolet Nexus spectrometer). Specimens were prepared by mixing 5 wt% of each sample with potassium bromide (KBr) and then pressing into a pellet. Transmittance spectra from  $4000$   $\text{cm}^{-1}$  to  $500$   $\text{cm}^{-1}$  wavenumbers were collected.

Download English Version:

<https://daneshyari.com/en/article/598872>

Download Persian Version:

<https://daneshyari.com/article/598872>

[Daneshyari.com](https://daneshyari.com)