



# A simple method to controlled synthesis of nano hydroxyapatite in different particle size



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## ABSTRACT

Synthesis processing factors are very important to impact on the performance of hydroxyapatite (HAP). The effect of the adding rate of the solution containing calcium and phosphor on the particle size of HAP was investigated in this paper. The results indicated that the particle size of HAP is controlled by the adding rate. A particle size of about 44 nm HAP is synthesized by the adding rate of 0.23 ml/s. The nucleation mechanism of HAP under the adding rates changing has been discussed.

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## 1. Introduction

Hydroxyapatite (HAP) has a wide range of applications in the field of environmental management and biomedical as a functional material [1,2]. Many previous works have shown that particle size has a great impact on the performance of HAP. Smaller HAP particle is more efficiently to reinforce the Young's modulus, yield and bending strengths of HAP-polyethylene composite [3,4]. However, more proteoglycan and collagen are deposited in the hydrogel-ceramic scaffolds with micro-HAP versus nano-HAP particles [5]. Nine crystalline HAP samples with different particle size were investigated to test the effect on TNF $\alpha$  secretion and engagement of the NF- $\kappa$ B pathway. The results indicated that tumor necrosis factor was decreased with the particle size increasing [6]. Small difference in the particle size of nano-HAP has a important significance in biomedical and environmental management applications [7–9]. The inhibition effect increased with HAP powder size decreasing and the cellular activity inhibition is 80% when 22 nm HAP particles was used as human colon carcinoma cells inhibition, and is better than the 11 nm HAP particles [7]. Zhang et al. [8] reported that 40 nm HAP were more cytotoxic towards MC<sub>3</sub>T<sub>3</sub>-E<sub>1</sub> compared with 70 and 100 nm HAP. Three particle-sized HAP were used for in the situ immobilization of Pb in low-acidity soil,

and HAP in the particle size of 20.08 nm has the best efficiency compared with 60.24 nm and microHAP [9]. Therefore, controlled the particle size of HAP is very important for perfectly show its function in application.

Synthesis temperature, aging time, reaction pH and calcination are the key factors for synthesized HAP's particles [10]. With the increasing of synthesis temperature and aging time, particle size of HAP is increasing [11–14]. The adding rate of raw materials for synthesizing HAP has been much less covered [10,14,15]. And the rage of adding rate was not detailed.

In this paper, high crystalline quality HAP was synthesized at room temperature, and the effect of the adding rate of raw material on the particle size of HAP has been investigated.

## 2. Experimental

HAP samples were synthesized by wet chemistry method, which is a simple solution process using phosphate acid [H<sub>3</sub>PO<sub>4</sub>], calcium nitrate [Ca(NO<sub>3</sub>)<sub>2</sub>] and ammonia [NH<sub>4</sub>OH] as raw materials. In a typical synthesis of HAP nanoparticles, calcium nitrate and phosphoric solution was added drop wisely respectively into ammonia solution at an additional rate under stirring (500 rpm), the additional rates are 0.007 ml/s, 0.08 ml/s, 0.23 ml/s, 0.56 ml/s and 2.5 ml/s, then stirring for 3 h. After aged 24 h, the reacted production was filtered to separate solid from liquid phase. All the steps described above are carried out at room temperature. Then the solid was washed with deionized water

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until the pH is 7 and dried at 105 °C overnight, followed by heat treatments with heating rate of 10 °C/min to 750 °C and calcinated at 750 °C for 2 h.

The morphology of HAP was characterized by field emission scanning electron microscopy (FESEM). The particle size was calculated from the picture of FESEM. And the phase purity as well as crystal structure of HAP were analyzed by X-ray diffraction (XRD, Cu K $\alpha$ ,  $\lambda$  = 1.54178 Å). The crystallinity of HAP was calculated from XRD.

### 3. Results and discussion

The XRD patterns of synthesized HAP powders are shown in Fig. 1. The main characteristic peaks at  $2\theta$  = 25.9°, 31.7°, 39.7°, 46.6° and 49.4° of HAP correspond to the standard XRD pattern of HAP(JCPDS 900-2215). It can be seen that the adding rate does not clearly affect the lattice parameters of HAP in the range from 0.007 ml/min to 2.5 ml/min from Fig. 1.

Fig. 2 exhibits the morphologies of HAP was characterized by FESEM which provided the basis for subsequent particle size analysis. The results shown that the particle size of HAP decreased with the increasing of the adding rate from 0.007 ml/s to 0.23 ml/s, and the smallest particle size of HAP is 44 nm at the adding rate of 0.23 ml/s. At the same time, the particle size of HAP was increased by the increasing adding rate after 0.23 ml/s.

The reason of the particle size changing by the adding rate may be the changing of the reaction pH and ions concentration in microenvironment at the reaction zone [16]. The  $K_{sp}$  of the reactants are shown in Table S1. In order to explore the relationship between  $1/K_{sp}$  and pH, the common logarithm of  $1/K_{sp}$  was calculated. The ions concentration of microenvironment varying by the pH is shown in Fig. S1. The chemical reactions occurred in the microenvironment are Eqs. (1)–(6).

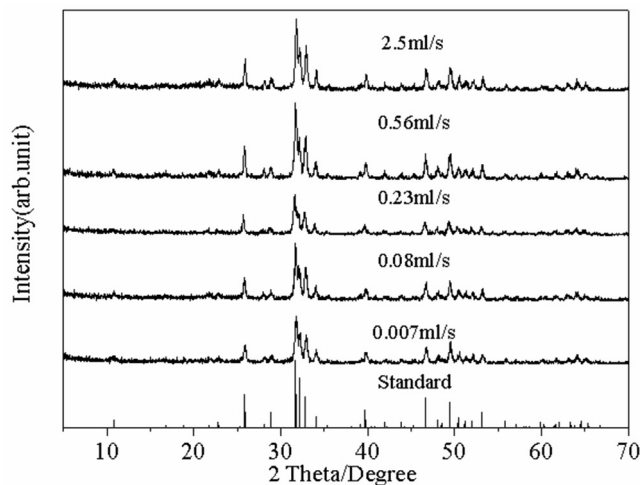
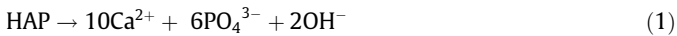
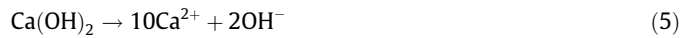
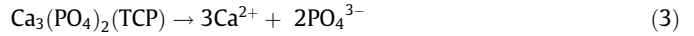


Fig. 1. The XRD patterns of HAP samples at different adding rates.



From the Eqs. (1) and (2), we know that the HAP would be produced if the value of  $1/((\text{Ca}^{2+})^{10} \times (\text{PO}_4^{3-})^6 \times (\text{OH}^-)^2)$  is equal or lower than that of  $1/K_{sp}(\text{HAP})$ , and it is the C1, C2 and C3 area shown in the Fig. S1. From the Eqs. (3) and (4), TCP would be produced if the value of  $1/((\text{Ca}^{2+})^3 \times (\text{PO}_4^{3-})^2)$  is equal or lower than that of  $1/K_{sp}(\text{TCP})$ , and it is the C2 and C3 area shown in the Fig. S1. From the Eqs. (5) and (6),  $\text{Ca}(\text{OH})_2$  would be produced if the value of  $1/((\text{Ca}^{2+}) \times (\text{OH}^-)^2)$  is equal or lower than that of  $1/K_{sp}(\text{Ca}(\text{OH})_2)$ , and it is the C3 area shown in the Fig. S1.

At low adding rates, the concentration of  $\text{OH}^-$  is enough,  $\text{Ca}(\text{OH})_2$ , TCP and HAP all can be produced in the first stage, and then the concentration of  $\text{Ca}^{2+}$  will decrease intensively, TCP and HAP would be produced. And then  $\text{Ca}^{2+}$  decreased to only HAP produced according to the Fig. S1. At the same time, the produced  $\text{Ca}(\text{OH})_2$  is reacting with  $\text{PO}_4^{3-}$  which ionized by the phosphoric acid and(or) TCP is reacting with  $\text{OH}^-$  which ionized by the rest ammonia. Thus more HAP produced following the stirring. So at this adding rate, the particle size of HAP is larger and the particle size composition is wider than the results of direct synthesized HAP. At high adding rates, because the concentration of  $\text{OH}^-$  is not enough in the microenvironment, no  $\text{Ca}(\text{OH})_2$  produced. TCP and HAP would be produced in the first stage, and then the concentration of  $\text{OH}^-$  will increase intensively, HAP would be produced only. At the same time, the produced TCP is reacting with  $\text{OH}^-$  which ionized by the rest ammonia. Thus more HAP produced following the stirring. So at this adding rate, the particle size of HAP is larger and the particle size composition is wider than the results of direct synthesized HAP too. At a moderate adding rate, the common logarithm of the reciprocal of the ion product of microenvironment is in C1 part (Fig. S1), only HAP may be produced. So at this adding rate, the particle size of HAP is the smallest and the size composition is uniform compared with that of other adding rate.

The nucleation models are shown in Scheme 1. According to the supplementary information, When the common logarithm of the reciprocal of the ion product is in C3 part, The intermediate ( $\text{Ca}(\text{OH})_2$ ) would be produced in homogeneous precipitation, and then produced HAP in heterogeneous precipitation, the similar to TCP. When the common logarithm of the reciprocal of the ion product is in C2 part, the intermediate (TCP) would be produced in homogeneous precipitation, and then produced HAP in heterogeneous precipitation. When the common logarithm of the reciprocal of the ion product is in C1 part, HAP would be direct synthesized in homogeneous precipitation, the particle size of HAP produced in homogeneous precipitation is the smallest. High purity HAP can be prepared by suitable concentration and suitable adding rate.

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