

# SYNTHESIS OF HYDROXYAPATITE AND APPLICATION IN BONE AND DENTAL REGENERATION IN HUMAN BODY

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## ABSTRACT

In the present work, hydroxyapatite (HAp) was successfully synthesized by wet precipitation method using  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and  $(\text{NH}_4)_2\text{HPO}_4$ , and  $\text{NH}_4\text{OH}$  as starting materials. The precipitate was dried by using freezer drier for 3 days and then calcined at  $800^\circ\text{C}$  for 1 hour. The powder sample was characterized by scanning electron microscopy (SEM), wide angle x-ray scattering (WAXS), IR and particle size analyzer. As a result, the HAp particle exhibited a micrometer-sized rod shape with a dimension of 0.55-1.2  $\mu\text{m}$  in diameter and 2.3-2.9  $\mu\text{m}$  in length, and the crystallinity increased after calcinations for Ca/P ratio of 1.66.

**Keywords:** *Hydroxyapatite; precipitation; crystallinity; bioceramic*

## 1. Introduction

Hydroxyapatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] is the most attractive and important bioceramics [1]. Due to its excellent biocompatibility and promising bioactivity with similar compositions and structures to bone and tooth minerals [2, 3, 4]. Various techniques have been developed to synthesize hydroxyapatite powders including mechanochemical synthesis [5], combustion preparation [6], and various techniques of wet chemistry. Such as direct precipitation from aqueous solutions [7, 8] electrochemical deposition [9], sol-gel procedures [10,11] hydrothermal synthesis [12,13] and emulsion or microemulsion routes [14,15]. Among them, chemical precipitation from aqueous solutions is a simple and versatile economic route, which was used in this study.

## 2. Experimental

### 2.1. Synthesis of HAp

HAp powder was prepared by chemical precipitation through aqueous solutions of the

reactants.  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{HPO}_4$  (99%, both supplied by Aldrich) were first dissolved in deionised water to form 0.5 and 0.5 M aqueous solutions, respectively. Equal amounts of these two aqueous solutions were mixed under magnetic stirring at room temperature. Ammonium hydroxide (Sigma Aldrich) was added immediately to adjust the reaction mixture to pH 10, which was kept constant throughout the experiment. After ripening for a specified period of time, the precipitates were recovered by centrifuge and then washed with deionized water. Five cycles of washing and centrifuging were repeated to ensure complete removal of the by-product.

The calcination of the synthesized powders was carried out at  $800^\circ\text{C}$  for 1 hour using a heating rate at  $3.0^\circ\text{C}/\text{min}$  in a tube furnace from room temperature to  $800^\circ\text{C}$  after drying the sample in freezer drier for three days.

### 2.2. Characterization

The phase composition and crystallinity of the “as-dried” and calcined HAp were analysed was examined by wide angle X-ray diffraction (Mac Science, Mac-18xhf). The

CuK $\alpha$  radiation ( $\lambda= 0.154$  nm) and curved graphite crystal monochromator were used in the measurement. The applied voltage and current of the X-ray tubes were 30 kV and 100 mA, respectively. Data were collected over the  $2\theta$  range 20-60 degree with a scanning speed of 5 degree/min. The morphology of the samples were analysed by scanning electron microscopy (Hitachi S-2140). IR spectra of the sample were collected in the range of 400-4000  $\text{cm}^{-1}$  by using model MATTSON 5000. Small amount of HAp powder were blended with KBr and then pressed into discs for the measurement. Particle size of HAp was measured by Zetasizer 1000HS.

### 3. Result and discussion

The infrared (IR) spectrum of HAp in Fig. 1 indicates that there are characteristic peaks of hydroxyapatite, corresponding to the stretching vibration of  $\text{PO}_4^{3-}$  (962.31; 1036.03; 1092.01) and deformation vibrations of  $\text{PO}_4^{3-}$  (565.24; 603.62) appear in the spectras. The weak absorption peak at 880  $\text{cm}^{-1}$  is assigned to the P-O-H vibration in the  $\text{HPO}_4^{2-}$  [20], which exists in non-stoichiometric HA. The C-O vibration in  $\text{CO}_3^{2-}$  group can also contribute to this absorption band. Peaks of H-O-H (3442.37; 1639.74) and  $\text{CO}_3^{2-}$  (1425.11) are also observed, the peaks at 2360.52 and 2341.22 come from  $\text{CO}_2$  in the air.

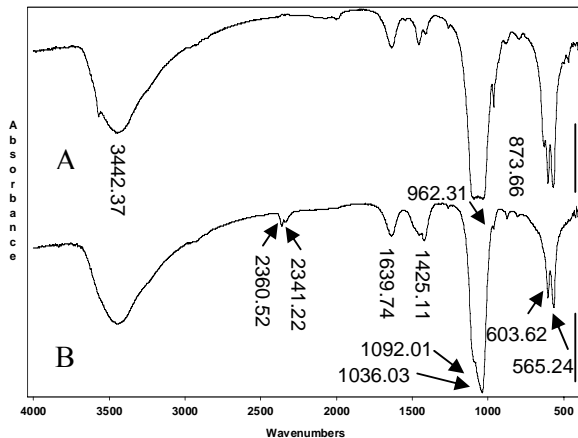


Fig. 1. IR spectrum of HAp precipitates obtained at pH=10; (A) as-dried, (B) calcined at 800°C for 1 hour

The bands at 3570 and 633  $\text{cm}^{-1}$  derived from stretching and vibration modes of hydroxyl in HAp [19] are nearly invisible in the spectras, which further implies that the HAp synthesized is quite weak crystallized.

The morphologies of the HAp powders precipitated at pH=10 were shown in Fig. 2.A, B. Before calcinations, the shape of HAp is not formed yet exhibiting high amorphous particles. After calcinations, rod shape is formed clearly.

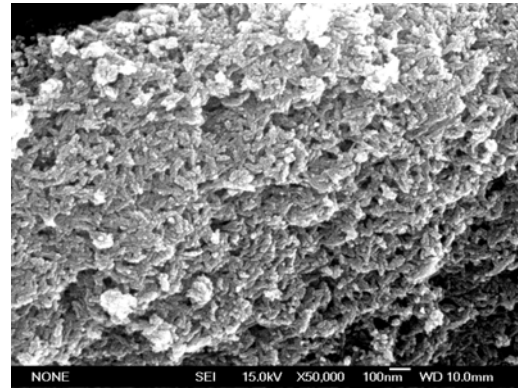


Fig. 2.A. SEM micrograph of the HAp precipitates obtained at pH=10-as-dried.

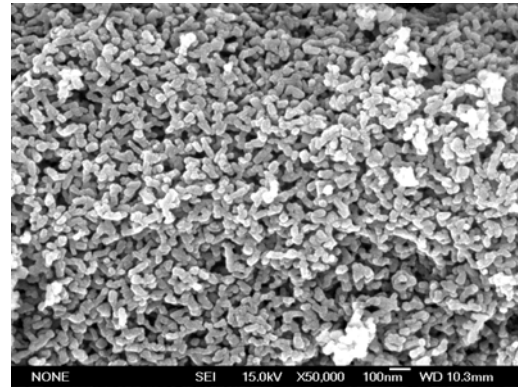


Fig. 2.B. SEM micrograph of the HAp precipitates obtained at pH=10-calcined at 800°C.

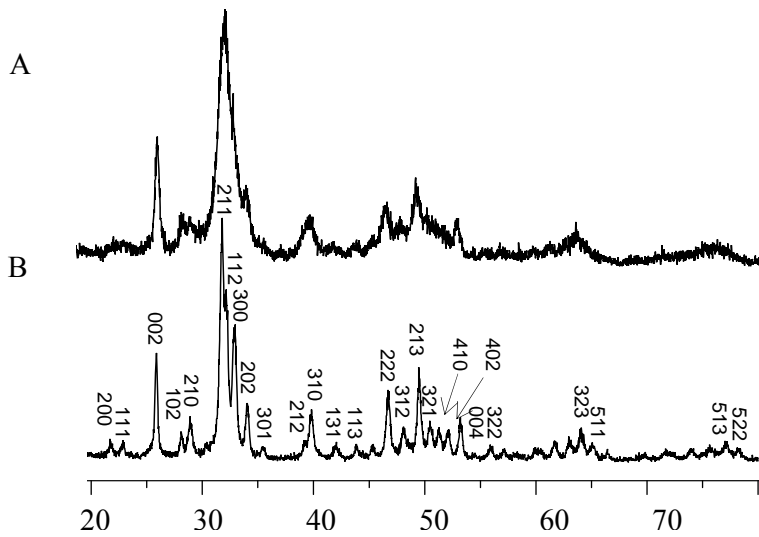


Fig. 3. XRD of HAp precipitates obtained at pH=10; (A) as-dried, (B) calcined at 800°C for 1 hour.

The XRD results show that the as-dried precursor is the poorly crystallized HAp in Fig.3 A. After calcinations at 800°C, the crystallinity is markedly increased in Fig. 3 B. The XRD spectra of all the synthesized HA powders closely matched with the ICDD PDF No: 9-432 of calcium hydroxyapatite, as the most clear evident of HA, the peak at 31.8°, corresponding to hydroxyapatite (2 1 1) peak of HA can be observed in Fig. 3B

Particle analyzer is shown in Table 1 and Fig. 4

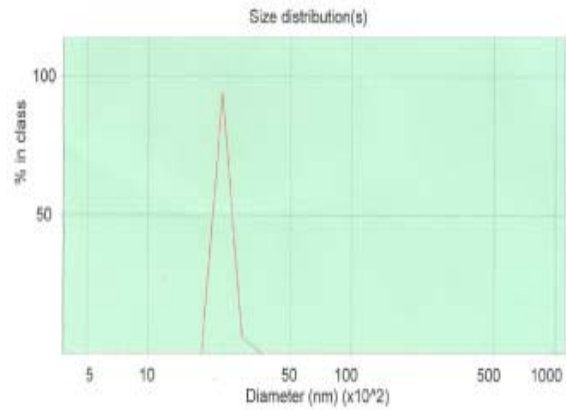


Fig. 4. Particle size distribution plot

Size(nm)	Intensity	Volume	Number
459.2	0.0	0.0	0.0
578.2	0.0	0.0	0.0
727.9	0.0	0.0	0.0
916.5	0.0	0.0	0.0
1153.9	0.0	0.0	0.0
1452.9	0.0	0.0	0.0
1829.2	0.0	22.8	23.8
2303.1	94.1	47.8	48.8
2899.8	5.9	27.2	26.2
3651.0	0.0	2.2	1.2
4596.8	0.0	0.0	0.0
5787.5	0.0	0.0	0.0
7286.9	0.0	0.0	0.0
9174.6	0.0	0.0	0.0
11551.3	0.0	0.0	0.0
14543.7	0.0	0.0	0.0
18311.3	0.0	0.0	0.0
23055.0	0.0	0.0	0.0
29027.5	0.0	0.0	0.0
36547.2	0.0	0.0	0.0
46014.9	0.0	0.0	0.0
57935.3	0.0	0.0	0.0
72943.7	0.0	0.0	0.0
91840.1	0.0	0.0	0.0

Peak Analysis by intensity			
Peak	Area	Mean	Width
1	100.0	2338.4	555.3

Peak Analysis by volume			
Peak	Area	Mean	Width
1	100.0	2387.4	1149.4

Peak Analysis by number			
Peak	Area	Mean	Width
1	100.0	2361.9	1111.8

Table 1. Particle size distribution data

#### 4. Conclusion

HAp was successfully synthesized by a chemical precipitation method. the HAp particle exhibited a micrometer-sized rod shape with a dimension of 0.55-1.2 μm in diameter and 2.3-2.9 μm in length, and the crystallinity increased after calcination for Ca/P ratio of 1.66.

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