

## Nano-size Hydroxyapatite Powders Preparation by Wet-Chemical Precipitation Route

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### Abstract

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In this study, wet-chemical process was performed to prepare nano-size hydroxyapatite (HA) powders ( $\approx 10$  nm) by varying concentration (low, medium and high) of the starting solutions in order to increase the amount of as-dried HA powders with different process conditions. Particle sizes and density were analyzed and differential thermal analysis was used to determine the glass transition ( $T_g$ ) and the onset crystallization ( $T_c$ ) temperatures. XRD and SEM were performed to identify phases and microstructure. The wet-chemical precipitation using low concentration of starting solution under reflux environment could be the optimize process to induce the formation of hydroxyapatite rather than tricalcium phosphate even though obtaining a smaller amount of as-dried powders compared to using high concentration. In addition, the density at  $4.05 \text{ g/cm}^3$  and specific surface area at  $89.58 \text{ m}^2/\text{g}$  as well as a uniform grain size morphology with a small size distribution can be achieved by using this route.

**Key words:** Hydroxyapatite, Wet chemical, Precipitation

### Introduction

Hydroxyapatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , HA] has been employed to produce substitute materials for the hard tissue implantation due to its excellent biocompatibility and osteoconductivity as well as close similarity to the human bone structure. Various processes for the preparation of HA powders have been developed over the past decades including wet synthesis<sup>(1-6)</sup> solid-state reaction<sup>(7, 8)</sup> and hydrothermal methods<sup>(9)</sup> etc. The initial purpose of these processes is to produce HA powders which demonstrate desired characteristics, for example high specific surface area, fine grain size and size distribution including small in particle agglomeration.<sup>(10)</sup> All these properties of HA powders depended on which process was performed. In particular, wet-chemical precipitation route is the most talented route owing to its ease in experiment operations, low working temperature, high percentages of pure products and inexpensive equipment requirement.<sup>(11, 12)</sup> The wet-chemical precipitation method was originally investigated by Jarcho and co-worker in 1976.<sup>(1)</sup> They succeeded in producing a dense polycrystalline hydroxyapatite with a high mechanical property. Later on several researchers developed and improved this method to achieve

better properties of hydroxyapatite ceramic.<sup>(1-6)</sup> Many factors influence the properties of hydroxyapatite by this method, for example starting materials, pH, stirring speed, temperature, ageing time, etc. In this study, to develop the HA properties, the concentrations of the starting solution were varied in refluxing process and a longer ageing time to increase the quantity of the products.

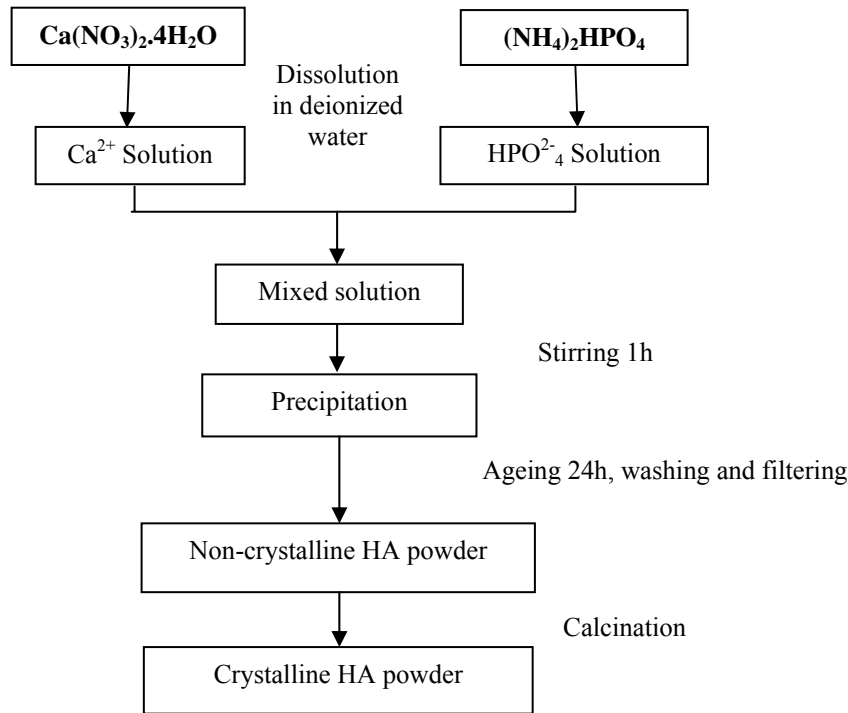
### Materials and Methods

The starting materials include:  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{HPO}_4$ . All reagents were of AR grade and used without further purification. Deionized water was used in all synthesis steps.

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{HPO}_4$  were dissolved in deionized water separately. The pH of each aqueous solution was adjusted to 11 by using  $\text{NH}_4\text{OH}$  solution 25%. The dropwise addition of  $\text{Ca}(\text{NO}_3)_2$  aqueous solution to vigorously stirred  $(\text{NH}_4)_2\text{HPO}_4$  solution at room temperature for about 1h produced a milky and somewhat gelatinous precipitate which was then stirred for 1h. Then the reflux process was employed at  $100^\circ\text{C}$  for 1h followed by ageing for 24h. It was then washed and filtered in a filter glass with

application of mild suction. Figure 1 and Table 1 explain the detail procedure and experimental conditions of HA powder produced by wet-chemical process. After filtration the compact, sticky filter cake was dried at 80°C overnight. As-dried powders were crushed by using mortar and pestle and calcined in alumina crucible at 800°C, 1000°C and 1200°C for 1, 2 and 4h.

to determine the glass transition ( $T_g$ ) and the onset crystallization ( $T_c$ ) temperatures by heating as-dried HA powders from room temperature to 1200°C at a heating rate of 10°C/min in alumina crucibles. To characterize phases before and after calcination a JEOL JDX 3530 diffractometer was used with  $\text{CuK}\alpha$  radiation ( $K\alpha = 1.5406 \text{ \AA}$ ) operating at 30 mA and 40 kV. XRD was



**Figure 1.** Modified chemical precipitation route for HA powder preparation. (Adapted from Sung [11])

**Table 1.** Experimental conditions of the samples studied in this work.

Method	Sample ID	Concentration
Reflux after mixing (Series 1, S1)	HA1	0.1 : 0.06 M
	HA2	0.5 : 0.3 M
	HA3	1 : 0.6 M
No reflux after mixing (Series 2, S2)	HA4	0.1 : 0.06 M
	HA5	0.5 : 0.3 M
	HA6	1 : 0.6 M
Excess reaction time to 48 hours (Series 3, S3)	HA7	0.1 : 0.06 M
	HA8	0.5 : 0.3 M
	HA9	1 : 0.6 M

## Materials Characterization

Particle sizes and density were analyzed by using Mastersizer and Ultracycrometer 1000, respectively. Differential thermal analysis was used

performed on powder samples. Spectra were obtained from 10 to 70° 2 $\theta$ , at a step size of 0.02° 2 $\theta$  and at a scanning speed of 2° 2 $\theta$ /min. The spectra were analyzed using JADE software and JCPDS cards. Scanning electron microscopy was performed to determine microstructure and crystal size of studied HA. The powder samples were carbon coated using a carbon evaporation coating unit. They were examined using a JEOL 6301F SEM operating at 20 kV with a working distance optimized for imaging and a large spot size.

## Results and Discussions

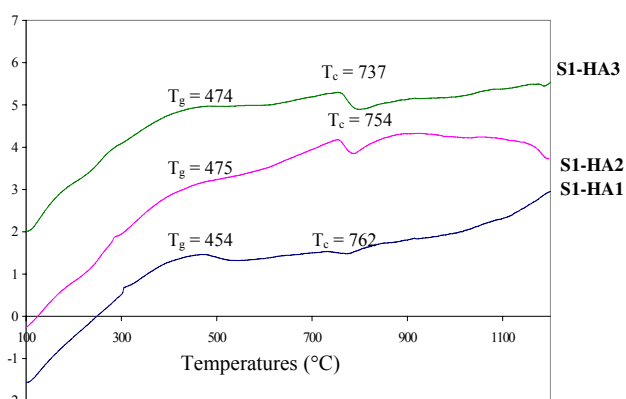
As-dried powders obtained from all series with low concentration provided a higher density over the samples with medium and high concentration. The highest of density 6.22 g/cm<sup>3</sup> was observed in the sample Series 2 with an

average particle size (after mortar and pestle applied) of  $\sim 20 \mu\text{m}$  as shown in Table 2. It could be explained that, the powders of all series tend to agglomerate. In addition, samples in all series with medium and high concentration provided a lower density compared to the sample with low concentration. The best specific surface area value is  $97.4 \text{ m}^2/\text{g}$  which was also observed in sample Series 2 with a high concentration, which was also greater than the one previously reported,  $79.8 \text{ m}^2/\text{g}$ .<sup>(13)</sup> However, the amount of as-dried HA powder synthesized by employing low concentration (0.1 : 0.06 M) was less than the amount of HA powders prepared by high concentration (1 : 0.6 M).

**Table 2.** Powder analysis results of as-prepared hydroxyapatite powders.

Sample ID	Mean Particle size ( $\mu\text{m}$ )	Density ( $\text{g}/\text{cm}^3$ )	Specific surface area ( $\text{m}^2/\text{g}$ )
S1-HA1	19.33	4.05	89.58
S1-HA2	26.64	2.92	-
S1-HA3	15.91	2.94	89.92
S2-HA4	20.83	6.22	80.49
S2-HA5	22.13	2.79	-
S2-HA6	4.48	2.81	97.4
S3-HA7	17.66	3.03	90.86
S3-HA8	22.06	2.84	-
S3-HA9	15.93	2.77	79.45

The DTA traces showed a broad dip corresponding to glass transition temperature ( $T_g$ ) of all series in a range of  $430^\circ\text{C}$  -  $480^\circ\text{C}$  and exothermic dips associated with crystallization temperatures ( $T_c$ ) of hydroxyapatite with tricalcium phosphate at a range of  $690^\circ\text{C}$ - $760^\circ\text{C}$  as presented in Figure 2 and Table 3.

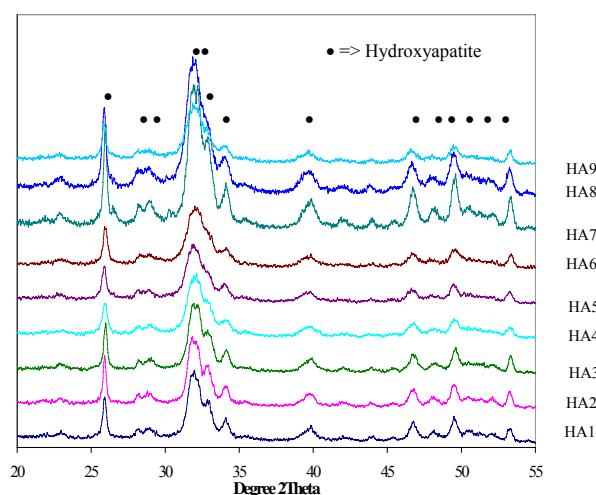


**Figure 2.** DTA traces of Series 1 samples.

**Table 3.** DTA results of as-prepared hydroxyapatite samples

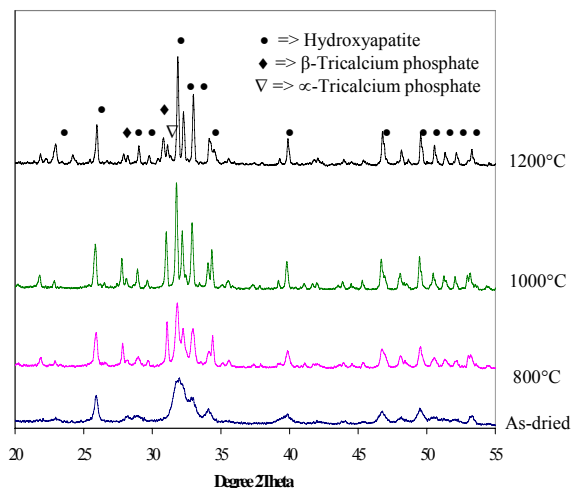
Sample ID	$T_g$ ( $^\circ\text{C}$ )	$T_c$ ( $^\circ\text{C}$ )
S1-HA1	474	737
S1-HA2	475	754
S1-HA3	454	762
S2-HA4	478	738
S2-HA5	445	755
S2-HA6	432	757
S3-HA7	448	753
S3-HA8	449	754
S3-HA9	480	687

Figure 3 presents XRD patterns of as-dried samples before calcinations, hydroxyapatite identified as the dominant phase in all samples.

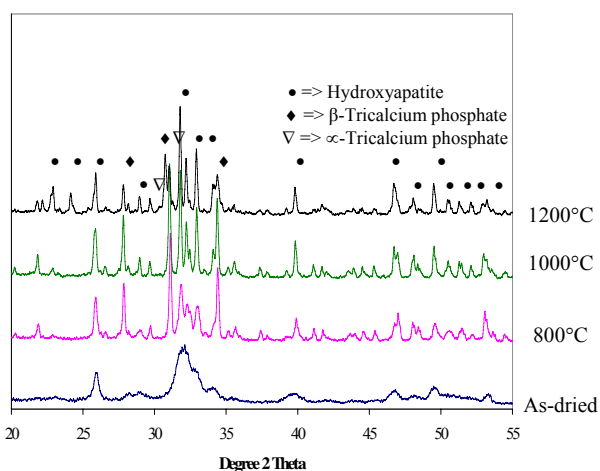


**Figure 3.** XRD Patterns of all as-dried HA powders

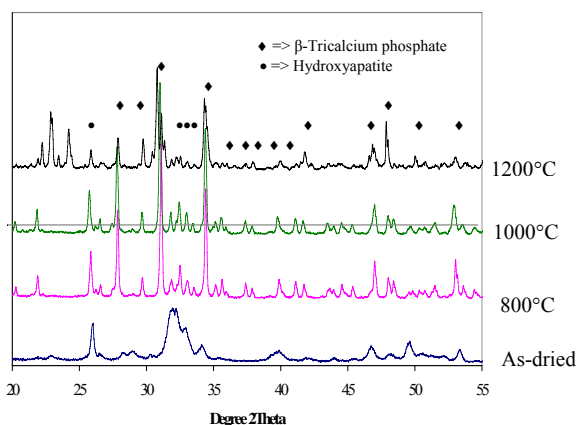
In the case of samples after calcinations, the dominant phase of hydroxyapatite with tricalcium phosphate as a minor phase was only observed in a sample of Series 1 with low concentration, Figure 4. Apart from this sample, tricalcium phosphate was indexed as a major phase with minor hydroxyapatite, Figures 5 and 6. In general, by wet methods larger quantity of HA can be produced, but there will be difficulties in achieving HA of stoichiometric composition.<sup>(14)</sup> Refluxing therefore induced water content which played a key role in hydroxyapatite formation during the preparation process as demonstrated in Series 1.



**Figure 4.** XRD Pattern of as-dried S1-HA1 and calcined at 800°C, 1000°C and 1200°C for 1 hour.

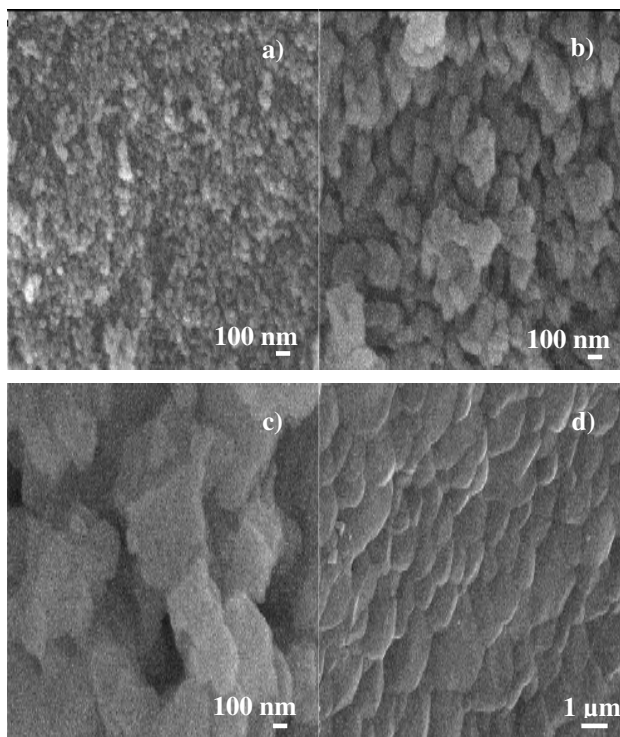


**Figure 5.** XRD Pattern of as-dried S2-HA4 and calcined at 800°C, 1000°C and 1200°C for 1 hour.



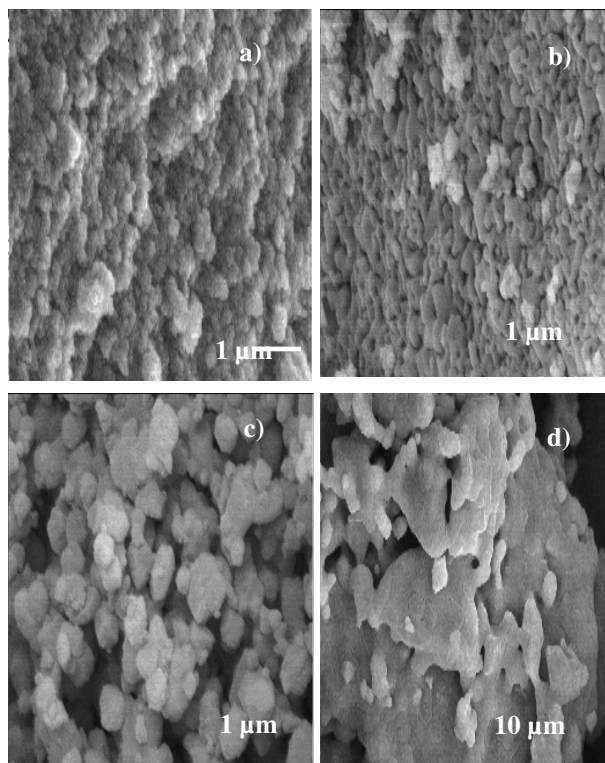
**Figure 6.** XRD Pattern of as-dried S3-HA7 and calcined at 800°C, 1000°C and 1200°C for 1 hour.

Small rod-like crystals (<100 nm) in the agglomerated particles were presented in as-dried HA powders of all series by SEM images. The uniform grain size with a narrow size distribution corresponding to the crystallinity improvement of the HA powders after calcination at 1200°C for 1h was illustrated by SEM, particularly in sample Series 1 with low concentration, Figure.7.

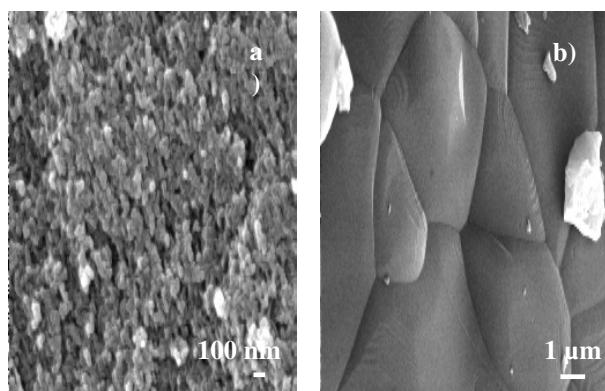


**Figure 7.** SEM images of S1-HA1 a) as-dried and calcined at b) 800°C c) 1000°C d) 1200°C for 1 hour.

In Series 2 and Series 3, the crystallinity of HA powder showed less improvement according to SEM images which presented only the connection of each particle with a small grain size due to the appearance of tricalcium phosphate as a dominant phase at 1200°C for 1h as illustrated in Figures. 8 - 9. Therefore, a lower calcined temperature (500°C -750°C) or longer calcined time is needed for Series 2 and Series 3 to induce the formation of hydroxyapatite.<sup>(15)</sup> In addition, SEM will be needed to examine the microstructure of samples with higher calcined temperatures over a longer period of time.



**Figure 8.** SEM images of S2-HA4 a) as-dried and calcined at b) 800°C c) 1000°C d) 1200°C for 1 hour.



**Figure 9.** SEM images of S3-HA8 a) as-dried and calcined at b) 1200°C for 1 hour.

Previously, LeGeros *et al.*<sup>(15)</sup> suggested that wet chemical precipitation method depends on the reactant concentrations and the pH of the reaction for HA formation. They also reported that HA produced through aqueous system by precipitation is usually calcium deficient and  $\text{HPO}_4^-$  enriched as shown by the expanded a-axis dimensions compared to mineral or ceramic HA and the formation of tricalcium phosphate or  $\beta$ -TCP phase upon heat treatment above 800°C.<sup>(4)</sup>

Therefore, it is not surprising that HA occurred coupled with tricalcium phosphate or the dominance of tricalcium phosphate with minor HA.

## Conclusion

For this study the wet-chemical precipitation by using low concentration of the starting solution under reflux environment could be the optimized process to induce the formation of hydroxyapatite rather than tricalcium phosphate, even though obtaining a smaller amount of as-dried powders compared to using high concentration. However, the density at 4.05 g/cm<sup>3</sup> and specific surface area at 89.58 m<sup>2</sup>/g as well as a uniform grain size morphology with a small size distribution can be achieved by using this route.

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