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# Nanosized hydroxyapatite powders derived from coprecipitation process

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Nanosized hydoxyapatite ($Ca_{10}(PO_4)_6(OH)_2$ or HA) powders were prepared by a coprecipitation process using calcium nitrate and phosphoric acid as starting materials. The synthesized powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) specific area measurment techniques. Single phase HA, with an average grain size of about 60 nm and a BET surface area of 62 $m^2/g$, was obtained. No grain coarsening was observed when the HA powders were heated at 600°C for 4 hours. HA ceramics were obtained by sintering the powders at temperatures from 1000°C to 1200°C. Dense HA ceramics with a theoretical density of 98% and grain size of 6.5 $\mu$m were achieved after sintering the HA powders at 1200°C for 2 hours. HA phase was observed to decompose into tricalcium phosphate when sintered at 1300°C. The microstructure development of the sintered HA ceramics with sintering temperature was also characterized and discussed. *© 2002 Kluwer Academic Publishers*

## 1. Introduction

Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$ or HA] has been extensively investigated because it is the main inorganic constituent of human bones and teeth [1]. Besides its significance in biology, HA is also a good candidate for applications in catalysts and ion exchangers due to its unique surface structure and ionic substitutions. Calcium-deficient hydroxyapatites with low Ca/P ratio possess electrical properties sensitive to environment at high temperature, making them potential candidates for applications in gas sensors and proton conductors [2]. Dense hydroxyapatite ceramics with good mechanical properties are required for practical application of bone substitution. The prerequisite for this purpose is to prepare HA powders which exhibit desired characteristics such as high specific surface area, small grain size with narrow size distribution and low degree of particle agglomeration. It is also noted that all these properties of HA powders are process-dependent.

Various processes have been employed to prepare HA powders, including chemical co-precipitation [3], sol-gel process [4, 5], spray-pyrolysis [6], hydrothermal syntheses [7], emulsion processing [8] and mechanochemical method [9]. Among these processes, chemical co-precipitation is the most promising method because of its simplicity of experimental operations, low operating temperature and high yields of pure products. Coprecipitation process was first proposed to prepare HA powders by Hayek and Newesely in 1963 [10]. The reaction of this process is presented as following:

$$\begin{aligned}&10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 8NH_3 \cdot H_2O\\&\quad = Ca_{10}(PO_4)_6(OH)_2 \downarrow + 6H_2O + 20NH_4NO_3 \quad (1)\end{aligned}$$

In this process, solution containing diammonium hydrogen phosphate was maintained at pH value greater than 12 by addition of ammonium hydroxide and then dropped into calcium nitrate solution with the same pH level. HA formation occurred during the mixing process. Based on this reaction, a very complicated process was developed by Tas *et al.* [11] for the preparation of hydroxyapatite-tricalcium phosphate (HA-TCP) composite powders. The prepared HA-TCP powders were reported to possess an average grain size of 600–700 nm. Other modifications, for example, replacing ammonium hydrogen with hexamethylenetetramine (HMT) [2], were also reported to prepare stoichiometric and calcium-deficient hydroxyapatites powders. However, preparation of nanosized HA powders via a coprecipitation process has been reported to be very difficult [12]. In the present work, a simple precipitation process, using $H_3PO_4$ instead of $(NH_4)_2HPO_4$, was proposed to prepare nanosized HA powders. The synthesized HA powders were characterized by XRD, SEM, BET measurements. HA ceramics from the powders were also obtained.

## 2. Experimental

A simple coprecipitation method was proposed in the present study to prepare nanosized HA powders using calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$] and phosphoric acid ($H_3PO_4$) as starting materials. $Ca(NO_3)_2 \cdot 4H_2O$ was dissolved in distilled water to form 0.5 M solution, into which $H_3PO_4$ was added with a Ca/P ratio of 1.67. After 30 minutes of mixing, ammonium hydroxide was poured into the mixed solution to precipitate HA. After stirring for 30 minutes, HA powders were obtained by washing the precipitate repeatedly to remove the unwanted ions ($NH_4^+$ and $NO_3^-$) and then drying at 70°C for 24 hours. The dried HA powders were also calcined at 400°C to 600°C for 4 hours to check the effect of temperature on the grain coarsening of the HA upon heating.

X-ray diffraction (XRD) analysis of the HA powders was carried out using a Rigaku ultima + type diffractometer with Cu $K_\alpha$ radiation and Ni filter. The average grain size of the HA powders was estimated using the Scherrer formula. The particle sizes were estimated on the basis of the Brunauer-Emmett-Teller (BET) specific surface area (Model ASAP 2000) using nitrogen as the absorption gas. The morphology of the powders was characterized using a JEOL JSM-6340F type field emission gun scanning electronic microscope (FEGSEM). The HA powders were then pressed uniaxially into 10 mm diameter pellets at a pressure of 50 MPa. The green pellets of about 70% of the theoretical density were sintered in a Carbolite RHF 1600 type furnace in air for 2 hour at temperatures from 1000°C to 1300°C with both heating and cooling rate of 5°C/min. The density of the HA ceramics was measured using a Mirage MD-200S type electronic densimeter. The microstructure of the sintered HA ceramics was characterized by FESEM.

## 3. Results an discussions

Figs 1 and 2 show the XRD patterns and SEM results for the as-dried and calcined HA powders. XRD pattern in Fig. 1a shows that well-crystallized single phase HA was directly precipitated via this process. The possible chemical reaction for this process may be expressed as follows,

$$\begin{aligned} &10Ca(NO_3)_2 + 6H_3PO_4 + 20NH_3 \cdot H_2O \\ &\quad = Ca_{10}(PO_4)_6(OH)_2 \downarrow + 18H_2O + 20NH_4NO_3 \quad (2) \end{aligned}$$

The grain size of the synthesized HA is estimated to be about 60 nm from the SEM observation with a narrow size distribution (Fig. 2a). Fig. 3 shows the nitrogen adsorption-desorption isotherm of the HA powders. The BET specific surface area of the synthesized HA powders is 62 $m^2/g$, resulting in a particle size of

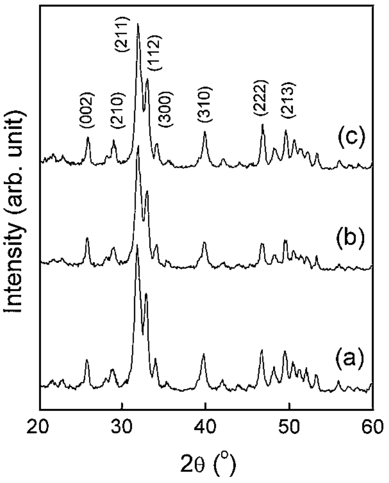

*Figure 1* XRD patterns for the as-dried (a) and calcined HA powders: (b) 400°C and (c) 600°C.

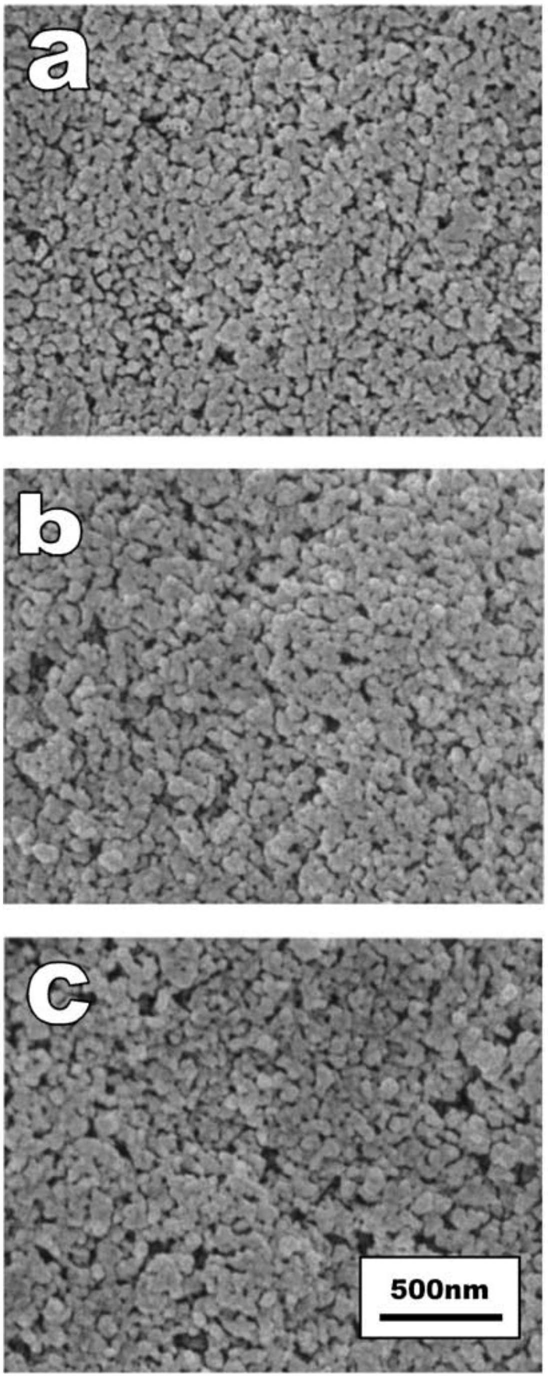

*Figure 2* SEM results of the as-dried (a) and calcined HA powders: (b) 400°C and (c) 600°C.

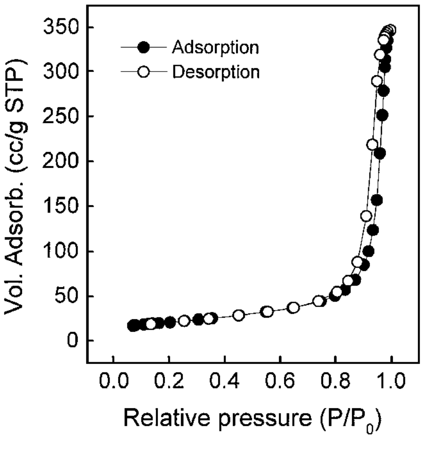

*Figure 3* Nitrogen adsorption-desorption isotherm of the HA powders.

about 32 nm through the empirical equation $t = 6/(\rho S)$ (where $t$ is the average grain size in $\mu$m, $\rho$ the density in g/cm$^3$ and $S$ the specific surface area in m$^2$/g). This size value is in general in agreement in terms of order of magnitude with that estimated form SEM observation. After annealing at 400°C and 600°C for 4 hours, no obvious changes in both morphology and grains size can be observed as can be seen in Fig. 2b and c. The property of the HA powders obtained in the present work is also found to be similar to that prepared by microemulsion method [8].

Precipitation of HA consists of two steps: nucleation and grain growth [13]. Nucleation is a process whereby molecules in solution randomly assemble to form aggregates which are not big enough to precipitate. Grain growth occurs when the nuclei become larger. When a solution contains more solute than should be present at equilibrium, the solution is called to be supersaturated. Parameter describing the degree of supersaturation of a solution is relative supersaturation, which is expressed as $(Q - S)/S$ (where $Q$ is the concentration of the solution and $S$ is the concentration at equilibrium [13]. The more solutes that are dissolved, the greater the supersaturation. It has been shown that relative super-saturation affects the rate of nucleation more than the rate of grain growth. That is, in a highly supersaturated solution, nucleation proceeds faster than grain growth. The result is a suspension of very tiny particles which leads to a small final size of the precipitate. Precipitation of HA involves $Ca^{2+}$ and $PO_4^{3+}$ simultaneously, both of which must be concentrated to favorite high rate of nucleation. The conventional precipitation of HA was conducted in such a way that either phosphorus solution was added into calcium solution or calcium solution was introduced into phosphorus solution. Precipitation in this manner in general does not meet the requirement of high rate of nucleation for HA. As a result, it is difficult to obtain HA with small grain size by the conventional precipitation process. In the present work, our mixture solution possesses high concentration of both phosphorus and calcium which promotes the formation of nanosized HA powders.

Fig. 4 shows the microstructure of the HA ceramics sintered at different temperatures. Fig. 5 shows the XRD patterns for the sintered samples. The variation in grain size of the HA ceramics as a function of sintering temperature is shown in Fig. 6.

The HA ceramics sintered at 1000°C for 2 hours have a density of 3.01 g/cm$^3$ (95% of the theoretical density 3.16 g/cm$^3$, ICDD 9-432) with an average grain size of 2 $\mu$m. As the sintering temperature is increased to 1100°C, the average grain size increases to 4 $\mu$m. The corresponding density is about 97% of the theoretical density. Further increase of the sintering temperature to 1200°C, results in a little increase in density (98% of the theoretical density), however, the average grain size increases rapidly to 6.5 $\mu$m. XRD results indicate that single phase of HA is maintained up to 1200°C as seen in Fig. 5c. For the samples sintered at 1300°C, the average grain size greatly increases to 12 $\mu$m. A slight drop in density is also observed at this sintering temperature. This may be attributed to the decomposition of HA to

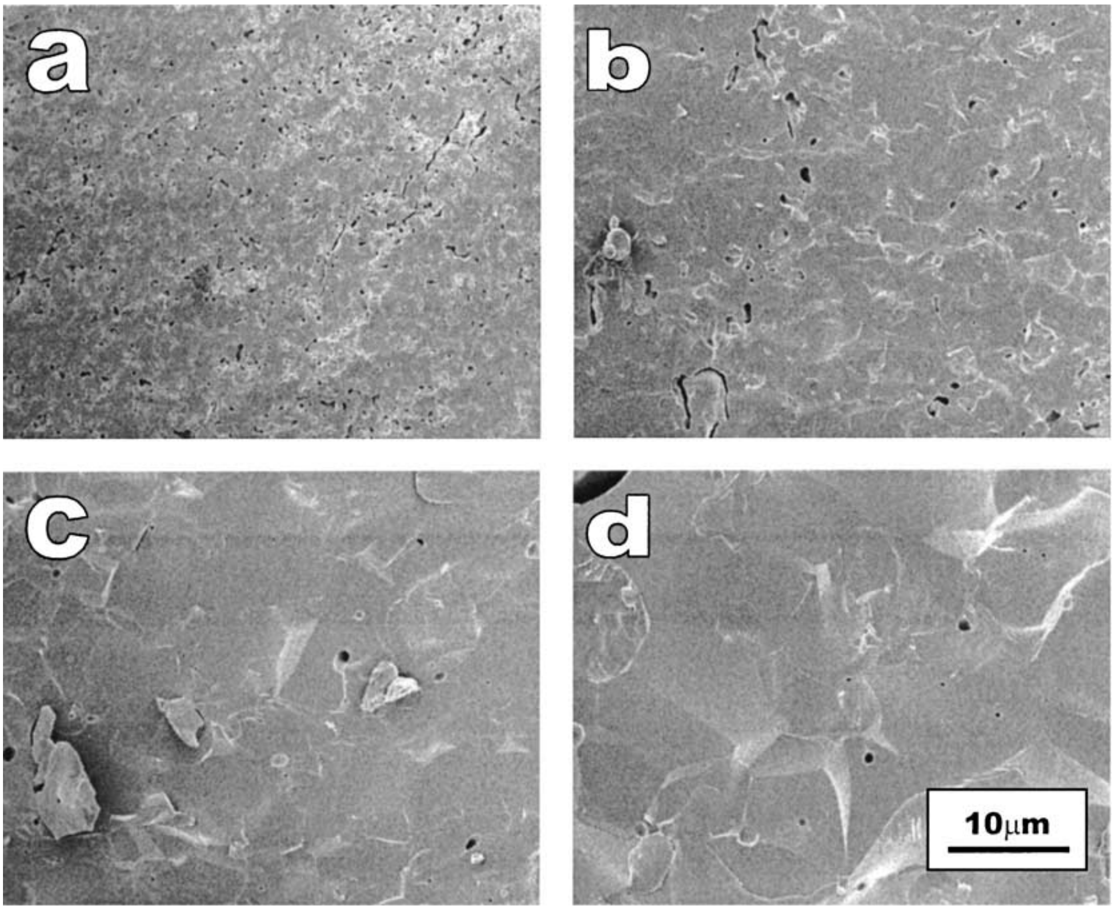

*Figure 4* SEM results of the HA ceramics sintered at different temperatures: (a) 1000°C, (b) 1100°C, (c) 1200°C and (d) 1300°C for 2 hours.

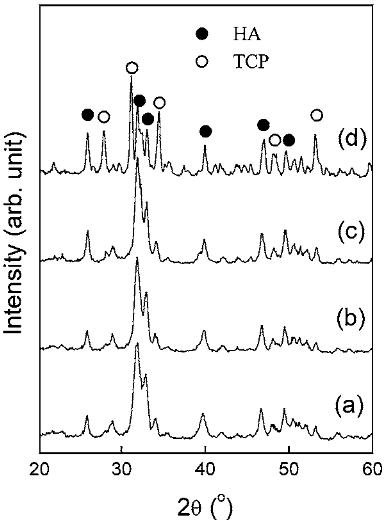

*Figure 5* XRD patterns for the HA ceramics sintered at: (a) 1000°C, (b) 1100°C, (c) 1200°C and (d) 1300°C for 2 hours.

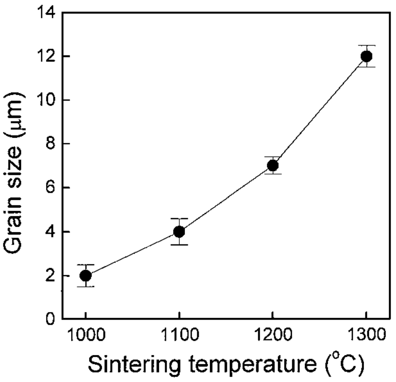

*Figure 6* Variation of grain size of the HA ceramics as a function of sintering temperature.

tricalcium phosphate ($Ca_3(PO_4)_2$ or TCP, ICDD 9-169) whose theoretical density is 3.07 g/cm$^3$, which is lower than that of HA (3.16 g/cm$^3$). The phase composition of HA to TCP is shown in Fig. 5d. This observation is also found to be in agreement with that reported in the literature [11].

Dense HA ceramics with uniform microstructures are desired for practical applications [4]. It is very hard to sinter conventionally derived HA powders below 1200°C. However, HA will decompose into TCP at temperature higher than 1300°C. To sinter HA at temperature higher than 1300°C without decomposition, sintering needs to be performed under moisture [14, 15]. Murray *et al.* [12] reported that HA powders derived from the conventional process could only be sintered to 80% at 1200°C for 2 hours. They did not mentioned the grain size of the HA powders but attributed the poor sinterability of the HA to agglomerates present in the conventionally processed powders. They also made an improvement in processing of HA ceramics by emulsion refinement. Varma *et al.* [16] developed a gel casting technique to improve sinterability of HA powders prepared by the conventional precipitation process, because they could not be well sintered via traditional processing. Compared to the reported results in the literature, HA powders prepared by the precipitation process in this work demonstrated good sinterability. This good sinterability can be attributed to the fine grains of the HA powders produced [17].

## 4. Conclusions

Nano-sized hydroxyapatite powders were prepared by a coprecipitation process from $Ca(NO_3)_2 \cdot 4H_2O$ and $H_3PO_4$. The average grain size of the HA powders produced were found to be 50–70 nm in size and showed no change when calcined at temperature up to 600°C for 4 hours. Dense HA ceramics were also obtained by sintering the synthesized HA powders at temperatures from 1000°C to 1200°C with a final average grain size of 2 to 7 $\mu$m correspondingly. The high sinterability of the HA powders is attributed to the fine grains of the powders produced in the present work. Decomposition of HA phase was observed at 1300°C sintering. It is believed that the process developed in the present work is also applicable for the preparation of other hydroxyapatite-based solid-state solutions.

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