SYNTHESIS AND CHARACTERIZATION OF NANO-HYDROXYAPATITE POWDER USING WET CHEMICAL PRECIPITATION REACTION

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The hydroxyapatite (HA) nano powder was synthesized via wet chemical technique in a precipitation reaction, in which Ca $(OH)_2$ and H_3PO_4 were used as precursors, respectively. Deionisked water as a diluting media for the reaction and ammonia as pH adjuster were used. The synthetic HA nano powder has been proved to have medical applications such as coating material in orthopaedic and dental implants. There has been studied HA powder at different temperatures from (100-800)$^\circ$ C to achieve the stoichiometric Ca/P ratio 1.667. The optimum temperature was found to be 600° C. Above this temperature, the HA powder is decomposed to CaO. The crystallite size of HA powder was found to be in the range 8.47-24.47 nm. The crystallographic properties have been evaluated by XRD, FTIR, EDX and SEM.

Keywords: Nano-HA powder; Chemical reaction, X-ray analysis

1. Introduction

Hydroxyapatite (HA) [$Ca_{10}(Po_4)_6(OH)_2$] is a naturally occurring mineral in the inorganic component of human bone and tooth enamel. The crystal size of HA in natural human bone is in nano range. The constituent elements of HA are primarily calcium and phosphorus, with a stoichiometric Ca/P ratio of 1.667. Hydroxyapatite (HA) is composed primarily of calcium and phosphorous with hydroxide ions that are eliminated at elevated temperatures. HA and other related calcium phosphate minerals have been utilized extensively as implant materials for many years due to its excellent biocompatibility and bone bonding ability and also due to its structural and compositional similarity to that of the mineral phase of hard tissue in human bones (Itokazu et al.1998;Minguez et al.1990). HA coatings have good potential as they can exploit the biocompatible and bone bonding properties of the ceramic, while utilizing the mechanical properties of substrates such as Ti_6-Al_4-V and other biocompatible alloys. While the metallic materials have the required mechanical properties, they benefit from the HA which provides an osteoconductive surface for new bone growth, anchoring the

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implant and transferring load to the skeleton, helping to combat bone atrophy (Liu, Y., et al., 2005). Their Ca/P ratio of 1.52±2.0 makes them an excellent choice for most dental and orthopaedic applications in the form of bioceramic coatings. The quality of a coating is closely dependent on the overall attributes and characteristics of the synthesized powders. Such attributes include phase composition, purity, crytsallinity, particle size, particle-size distribution, specific surface area, density and particle morphology. These important factors determine the resulting success of the HA coating deposited onto orthopaedic implants through plasma thermal spraying due to poor mechanical properties of HA the recent trend in bioceramic research is focused on improving their mechanical and biological properties using nanotechnology(K.P.Sanosh et al.2009). Common methods used to produce synthetic nano-crystalline HA include precipitation (Saeri et al., 2003), hydrothermal (Masahiro et al., 1994), hydrolysis (Shih et al., 2004), mechanochemical (Silver et al., 2003) and sol gel (Kim and Kumata, 2004).

In the present work nano-sized HA powder was synthesized via wet chemical precipitation method using calcium hydroxide, orthophosphoric acid and ammonia as precursors.

2. Experimental

In the present work, calcium oxide (CaO)(Make S d Fine Chem Limited), orthophosphoric acid (H_3PO_4) (Make Fisher Scientific), and ammonium hydroxide (NH_4OH) (Make Fisher Scientific) were used as starting materials. Firstly, an analytical weighing scale was used to accurately weigh CaO powder. 1.42 mol (79.55g) CaO powder was added to 500 ml of deionised water in a 1000 ml beaker and vigorously stirred at 1000 rpm at the 20° C for 24 hrs to react and form a suspension of $Ca(OH)_2$ in an excess of deionised water. The beaker was covered in order to avoid possible contamination via contact with atmospheric conditions. The temperature of the reaction (20° C) was maintained by a thermostat-controlled water bath.

An analytical weighing scale was used to accurately weigh the required quantity of orthophosphoric acid. 97.32g of 85% H_3PO_4 was added to Ca $(OH)_2$ solution at a rate of 1.5 ml/min. During the course of the acid addition, the pH of the solution was monitored via a handheld pH meter with an accuracy of ± 0.2. The reactants were stirred for further 24 hrs to aid the maturation stage, under continuous stirring conditions at 1000 rpm, held at the respective reaction temperature of 20^0 C. 0.28 mol (9.94g) NH_4OH, was added to the HA slurry after 24 hrs ripening period to stabilise the pH of the super saturation solution to above 9.

Assay samples were taken for analysis of the composition of mixture in the barrel. A small crucible was filled with a sample of the mixture in the mixing barrel and dried in a drying oven for 1hr at 100° C. The dried samples were then placed in a furnace and sintered at 1200° C for 1 hr. When the assays were cooled, they were removed from the furnace and ground using a motor and pestle. Scanning electron microscopy (SEM) (HITACHI model S-3700N at DTU) was used to observe the morphology and the particle size of calcined HA powder. Elemental phase composition of the HA powder was analysed using energy dispersive X-ray (EDX) (HITACHI model S-3700N at DTU). The X-ray diffraction (XRD) pattern of the final HA nanoparticles was obtained with CuKα radiation (λ= 1.5406 Å) on (RIGAKU MINIFLEX at AMU). The XRD patterns were recorded in the 2θ range of 20^{o} -60° with a step size of 0.02° and a step duration of 0.5 sec. The mean crystallite size (D) of the particles was calculated from XRD line broadening measurement using the Scherrer equation (Azaroff, 1968):

$$\boldsymbol{D = \frac{0.89\lambda}{\beta cos\theta}}$$

where λ is the wavelength CuKα , β the full width at half maximum of the HA line and θ the diffraction angle.

3. Results and discussion

The following reactions were involved in the formation of HA during the precipitation reaction: b

$$CaO + H_2O \longrightarrow Ca(OH)_2 \quad (1)$$

$$10Ca(OH)_2 + 6H_3PO_4 \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O \quad (2)$$

Fig. 1 shows the XRD pattern of HA from 100°-800° C. The crystallite size calculated by Scherrer equation with most intense plan that is 211 of eight calcined HA samples for each temperature are given in table 1.

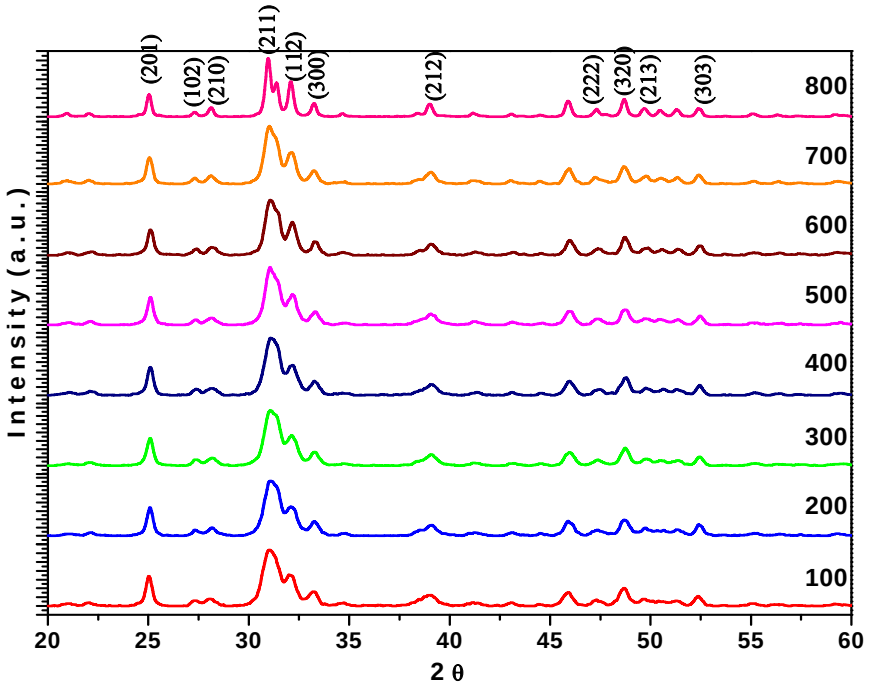

Fig. 1. XRD patterns of HA powders calcined at different temperatures

Table 1

Crystallite size at different calcination temperatures

S. No.	Different Calcination Temperature (^{0}C)	Crystallite Size D (nm)
1	100	8.4
2	200	12.1
3	300	12.4
4	400	12.6
5	500	14.5
6	600	14.5
7	700	14.6
8	800	24.4

It can be observed that with the increase in the calcination temperature the crystallite size also increases. Similar phenomenon was observed by Bouyer et al. (2000) and K.P.Sanosh et al. (2009). It has also been reported that HA calcined at higher temperatures exhibiting good crystallinity. Also, it shows little or no activity towards bioresorption which is important for the formation of chemical

bonding with surrounding hard tissues (Aoki, 1994, Currey, 2001 and K.P.Sanosh et al., 2009). Thus the amorphous HA powders that were obtained at lower temperatures in this study are expected to be metabolically more active than the fully developed crystalline hydroxyapatite structure which otherwise is insoluble in physiological environment (Kim et al., 2000 and K.P. Sanosh et al., 2009).

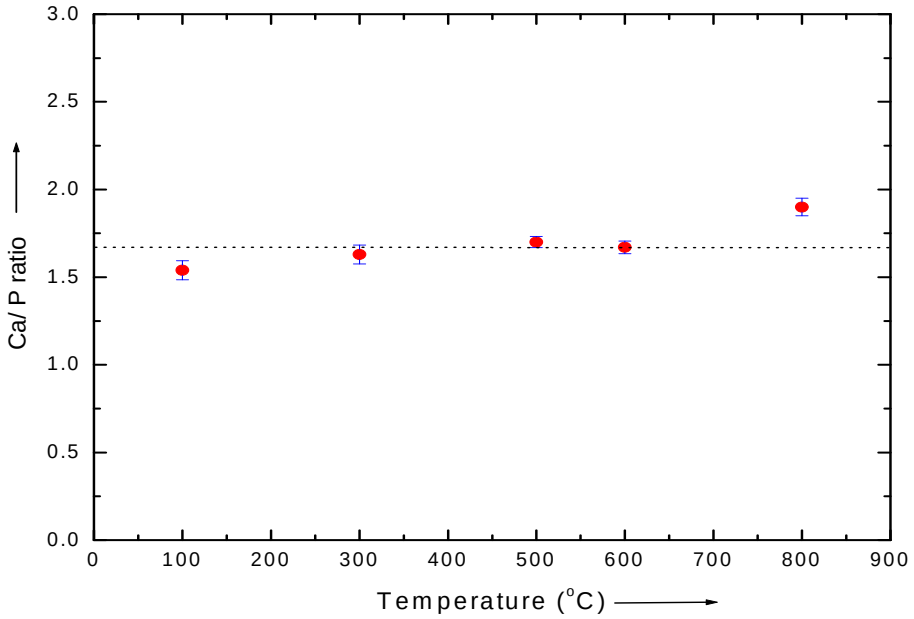

Fig. 2. Plot of variation of Ca/P with calcinations temperature

The XRD spectra of the different calcinated HA powders studied are shown in figure 1. The spectra found are typically in agreement with those published in literature; all XRD spectra obtained have characteristics peaks consistent with the International Centre for Diffraction [JCPDS 2001] files for calcium phosphate. The predominant HA phase was confirmed with JCPDS files number 09-432.

This suggests that no foreign elements, such as sodium (Na^{2+}), ammonium (NH_4^+), potassium (K^+), chloriode (Cl^-) and nitrate (NO_3^-) ions, were involved in the synthesis reaction, as there is strong evidence to suggest that these ions are easily incorporated into the crystal lattice leading to the formation of known stoichiometric HA. These elements are usually introduced into the precipitating systems with the reactants. The absence of these elements can be attributed to the nature of the raw materials used as precursors. In fact, it has been shown that chloride ions enter into the crystal lattice substituting hydroxyl groups while

potassium ions are found to substitute calcium ions into the HA crystal lattice forming locally non-stoichiometric (i.e. impure) HA islands in the bulk crystal. Sodium ions also show evidence of substitutions. In order to avoid contamination of the products, use of calcium nitrate and phosphoric acid instead of calcium chloride salts and potassium dihydrogen phosphate, respectively is advantageous because the presence of potassium ions is avoided and the nitrate ions are too large to substitute hydroxyl groups in the crystal lattice of HA. These substitutions were avoided while preparing our samples when $Ca(OH)_2$ and H_3PO_4 reactants were used. For all of the HA studied no CaO was observed. This indicates that there has occurred either small or no carbonation of HA during the synthesis of HA tested although no foreign element were found.

The Ca/P stoichiometry of calcined HA at different temperatures was analysed using EDX.

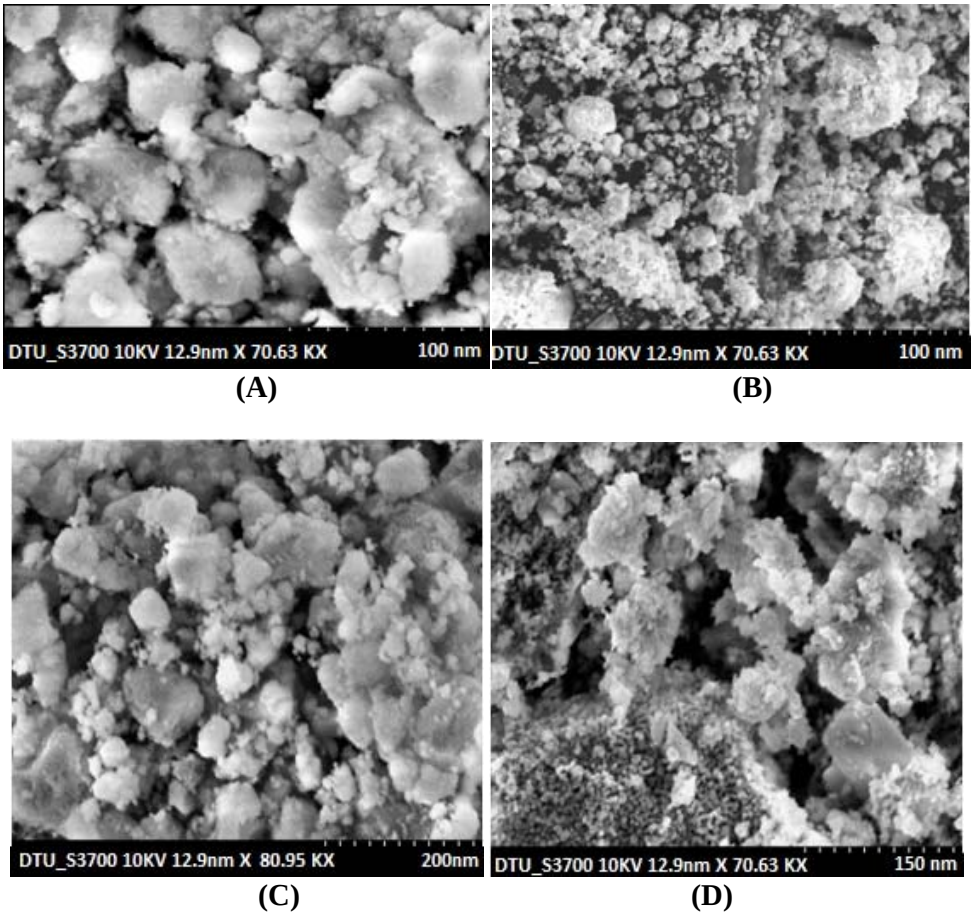

Fig. 3: SEM images of HA Powder at different temperatures

Analysis of figure 2 shows that HA powder with a Ca/P ratio near to 1.67 that is at temperature 600° C and below, showed no CaO content and that with a Ca/P ratio near to 1.75 and above, showed the formation of minor amounts of CaO for calcined samples at 800° C.

Other researchers have also reported similar formation of CaO in sol-gel processing of HA (Lopatin et al., 1998, Varma et al., 1998 and Sanosh et al., 2009).

SEM was performed at Delhi Technical University (DTU), Delhi in Nanoscience and Technology Centre. The sample (HA) is coated with gold and placed in the SEM machine (HITACHI MODEL-S-3700N). The images were recorded at different temperatures ranging from 100- 800° C. It is known that spherical powders, in general, have better rheological properties than irregular powders and, thus, produce better coatings for hip implants. In order to produce dense, high-quality materials for special-purpose, it is very important to predict or control granule morphology. Kothapalli et al. also demonstrated that an increase in synthesis temperature increases the size of HA precipitates.

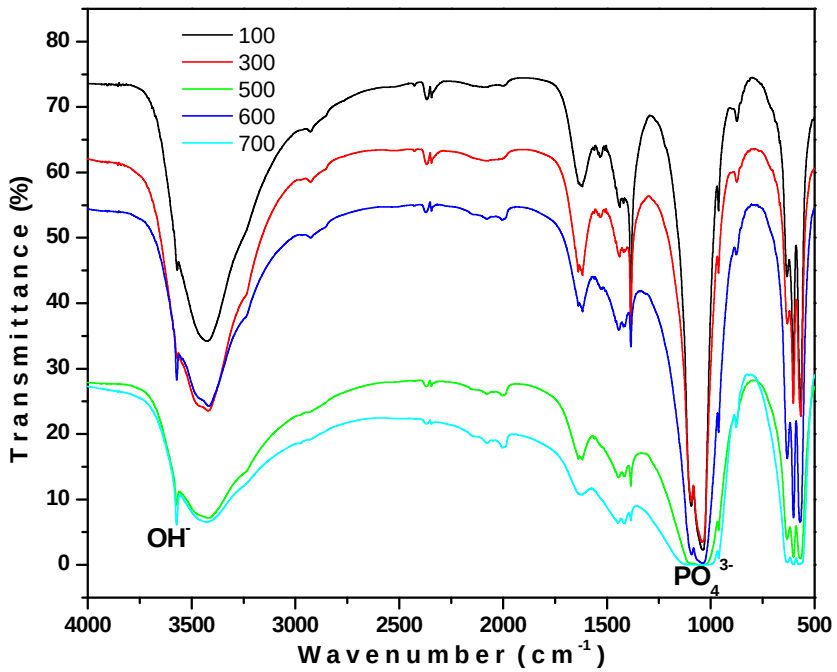

Fig. 4. FT-IR spectrum of HA calcinated at different temperature

FT-IR patterns presented in figure 4 confirm the formation of HA calcinated at different temperature 100-700° C. The spectra possessed an $(OH)^{-1}$ group in the region of 3577 cm^{-1} and $(PO_4)^{3-}$ group comes out in the region of 1075 cm^{-1}. From this analysis the formation of HA is confirmed. The peaks are quite sharp at intermediate temperatures (500-600° C) and as the temperature increases peaks are going to be weak as shown in figure 4.

4. Conclusions

The above presented work used the wet chemical precipitation method due to its high reproducibility, simplicity and also on account of the economical benefits it offers on industrial scale. One of the main advantages of the method is that the water is its only byproduct. The reported method used calcium hydroxide and orthophosphoric acid as precursors. This process shows that high purity of nano-hydroxyapatite powders could be obtained at low temperatures. The crystallinity, crystallite size and Ca/P ratio of the resulting nano particles were found to be dependent on the calcination temperature. When Ca/P ratio exceeded 1.75, formation of CaO phase was observed.

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