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The facile and phase pure evaluations of nano Hydroxyapatite powder by sol-gel method.

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Abstract : A bioactive ceramic such as hydroxyapatite [HAP: $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] is a versatile ceramic material and which can be used in dental and orthopedic applications due to their excellent behaviour in the human body. The present investigation is aims to synthesis nano sized HAP by sol-gel method using different calcium sources such as calcium acetate and calcium nitrate with orthophosphoric acid as a phosphorus precursor respectively. These initial reactants are easily available and low cost reagents for the preparation of HAP powder. The calcium acetate with orthophosphoric acid leads to biphasic calcium phosphate which contains major phase as HAP and minor phase as β -TCP with respect to different sintering temperatures. The calcium nitrate and orthophosphoric acid has produced, pure nano sized HAP without accompanying any other secondary phases at higher temperature treatments. The phase purity and crystallinity of HAP was improved with increasing in the heat treating process. The materials prepared from both calcium sources and orthophosphoric acid was subjected to characterize by powder XRD, FT-IR, SEM.

Keywords: Hydroxyapatite; sol-gel method; Tri Calcium Phosphate; acetate; nitrate.

Introduction

Synthetic Hydroxyapatite has been one of the most widely used biomaterial for repairing hard tissues and scaffold for tissue engineering in biomedical applications owing to its natural bone mineral properties such as bioactivity, biocompatibility and osteoconductivity¹⁻². Synthesized HAP has involved in different types of clinical applications as coatings for metallic orthopedic and dental implants for better bonding with human bone and thus increasing life time of the implants³. However HAP shows poor in mechanical strength and unable to use for heavy load bone bearing applications, to improving its mechanical strength the composites have been developed with biopolymers and carbon based biomaterials⁴⁻⁵.

Natural bone apatites are in the range of nano-sized with a very large surface area to volume ratio and ultra fine structure. These apatite crystals are reinforced in an organic matrix and have very loose crystal to crystal bonds. Therefore, the resorption by osteoclasts is quite homogeneous. Synthetic HAP crystals are in nano to submicron size with low surface area and have strong crystal-to-crystal bond. The natural apatite exhibits faster bone formation compared with conventional HAP⁶.

In recent years several methods have been developed for the synthesis of HAP with pure phase and desired surface morphology. Sol-gel method is a promising technique for the preparation of nano sized HAP using different calcium and phosphorus sources such as calcium acetate, calcium chloride, calcium nitrate, triethyl phosphate, triethyl phosphite, phosphorus pentoxide etc.,. The major limitation of the sol-gel process is associated with the rate of hydrolysis activity of phosphates, time consuming and the more cost of the precursor materials. These complications were tried to solve in this proposed paper. In this paper nano scale HAP was generated by using inexpensive non-organometallic calcium and phosphorus sources such as calcium acetate, calcium nitrate and Orthophosphoric. In another hand the pH was adjusted with aq. NH_3 .

The aim of the present work is to synthesize nano pure HAP powder at lower temperature for orthopedic and dental applications.

Experimental

The HAP was synthesized via sol gel method using different calcium sources with same phosphorus source and the preparative process was described as follows.

Method-1

The calcium nitrate tetrahydrate and orthophosphoric acid were taken as calcium and phosphorus sources respectively and dissolved them in double distilled water. A stoichiometric amount of calcium nitrate tetrahydrate was slowly added to the phosphorus solution in order to obtain a Ca/P ratio of 1.67, under vigorous stirring the pH was adjusted as 10 by adding aq NH_3 . After complete addition of the sources to each other, stirring process was continued for 1h. The obtained white colloidal suspension was aged for 24 h. Aged suspension was dried at 100 °C and repeatedly washed with DD H_2O to maintain the pH neutral. The gel was dried at 100 °C and dried raw powder was ground and sintered at 500, 700, 900 and 1000 °C for 2 h.

Method-2

The calcium acetate and orthophosphoric acid were taken and dissolved in DD H_2O . To maintain Ca/P ratio 1.67 the raw materials were added each other. The remaining preparation parameters are similar as described as above to synthesize of nano HAP.

Characterization

The as dried and sintered powder were characterized by Fourier transform infra red spectroscopy (FT-IR) in the range of 400–4000 cm^{-1} using SHIMADZU model spectrophotometer, for functional groups identification. To investigate the phase identification and crystallinity of sintered powder was done by using Bruker D8 Advance X-Ray Diffractometer, with a step size of 0.02 and using Cu $\text{K}\alpha$ (1.5406Å), and Ni filtered radiation. Surface topography of HAP and its particles shape and size was observed by Scanning electron microscopy (SEM).

Results and Discussion

Fourier Transformer Infrared Spectroscopy (FT-IR)

The FTIR spectrum of calcium acetate based raw powder sintered at different temperatures are illustrated in Fig.1. The IR spectrum confirms the presence of characteristic peaks for the identification of functional groups in HAP. In IR Spectra a very weak band at 3642 cm^{-1} and strong band at 634 cm^{-1} are corresponds to the presence of OH^- group. The absorption band at 1638 cm^{-1} belongs to the stretching mode of H_2O molecules. The broad band at 1053 cm^{-1} and sharp bands at 606, 570 and 473 cm^{-1} are assigned to the presence of PO_4^{3-} in HAP. The strong vibration bands at 1459 and 873 cm^{-1} are belongs to the CO_3^{2-} in HAP crystal lattice, which are due to incompletely pyrolyzed organics from atmosphere and interacts with HAP.

The Fig.2 represents the calcium nitrate based HAP sintered at different temperatures. The representative FTIR spectra of synthesized HAP have shown all characteristic absorption peaks of pure HAP. The main identification for the formation of pure HAP in IR spectra are found in three regions they are (i) the band at 3570 cm^{-1} and the vibration band at 646 cm^{-1} are originated from OH^- group. (ii) The bands at 961 cm^{-1} are characteristic bands of PO_4^{3-} ions (ν_1 band), 1111 and 1042 cm^{-1} (ν_3 band) and 560 and 603 cm^{-1} (ν_4 band).

(iii) The presence of 1441 and 873cm^{-1} peak confirms the presence of carbonate group⁷. These IR results were further evidenced by powder-XRD analysis.

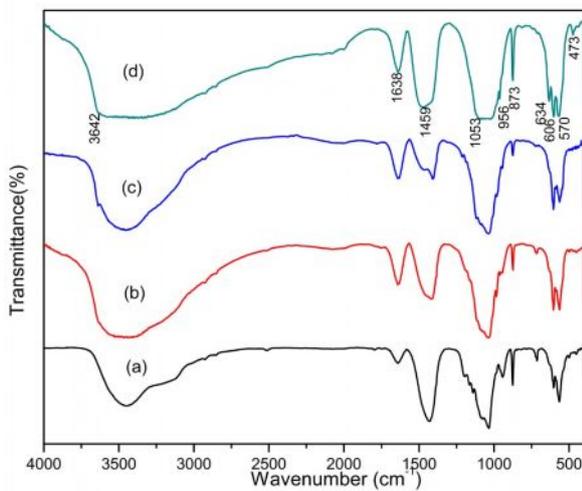


Fig.1. FTIR spectra of calcium acetate based HAP sintered at (a) 500 (b) 700 (c) 900 (d) 1000 °C for 2 hr

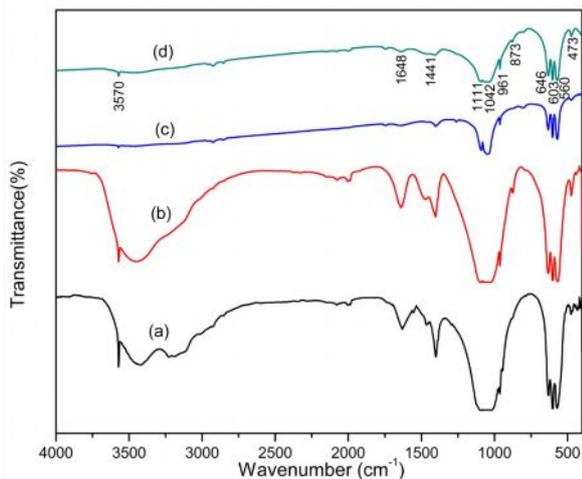


Fig.2. FTIR spectra of calcium nitrate based HAP sintered at (a) 500 (b) 700 (c) 900 (d) 1000 °C for 2 hr

Powder XRD

To study the process of crystallization, the raw powder was sintered at four different temperatures namely, 500, 700, 900 and 1000 °C. The XRD patterns of calcium acetate synthesized HAP shown in Fig.3. From Fig.3 represents the raw powder sintered at 500 °C and it appear as a formation of amorphous HAP with broad diffraction peaks. As the sintering temperature increased, the peaks are become more distinct with narrow width and the degree of crystallinity increased. And it can also be seen that the additional crystalline peaks were observed at 27.6 , 29.3 , 31.07 and 34.35° which are corresponds to the presence of impurity phase of β -TCP (JCPDS No. 29-0359). The high intensity diffraction peaks of β -TCP are gradually decreased with increase in heat treatment (700 to 1000 °C) and found to be less impurity accompanying phase of HAP (JCPDS No. 009-0432).

Fig.4 shows the XRD pattern of calcium nitrate based HAP. The diffraction peaks of intensity and positions of synthesized HAP are exactly matched with the parent pattern of HAP (JCPDS No. 009-0432). The crystallinity nature of HAP at 500 and 700 °C found to be as lesser while compare with 900 and 1000 °C and no other secondary phases were observed along with HAP. It indicates that the sintering treatment plays a significant role on the formation of pure nano HAP.

The average crystallite size (D) of nano HAP was estimated from the full width at half-maximum (FWHM) of the powder XRD pattern using Scherrer's formula.

$$D = k\lambda/B \cos\theta$$

Where λ is the wavelength of X-ray, θ the Bragg angle, k is the constant depends on the grain shape (0.89 \AA for circular grains). The calculated average crystallite size of the all sintered HAP samples are shown in Table.1.

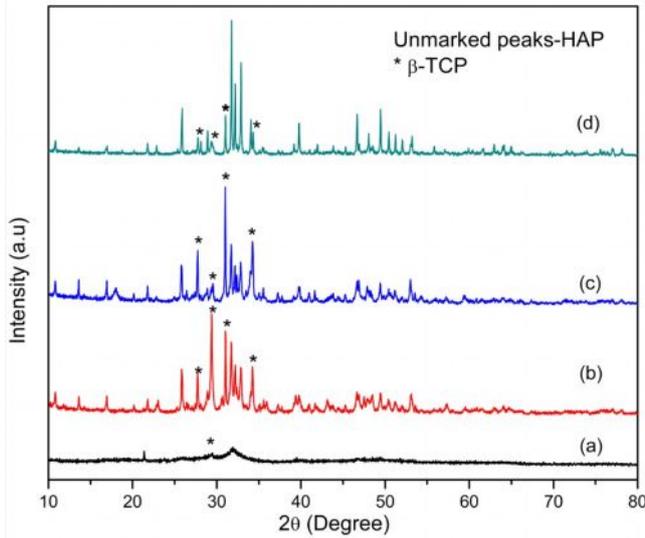


Fig.3. XRD pattern of calcium acetate based HAP sintered at (a) 500 (b) 700 (c) 900 (d) 1000 °C for 2 hr

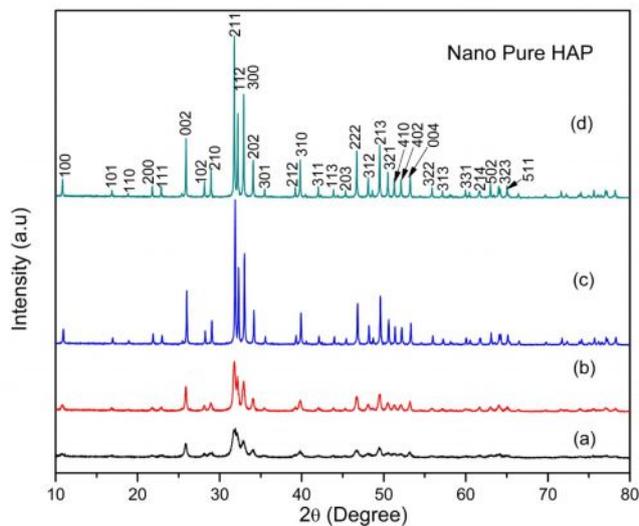


Fig.4. XRD pattern of calcium nitrate based HAP sintered at (a) 500 (b) 700 (c) 900 (d) 1000 °C for 2 hr

Table.1. Calculated average particle size from Scherrer formula

S.No	Calcium acetate based HAP		Calcium nitrate based HAP	
	Temperature (°C)	Crystallite Size D (nm)	Temperature (°C)	Crystallite Size D (nm)
01	500	68 ± 1.2	500	32 ± 1.6
02	700	85 ± 2.5	700	48 ± 2.1
03	900	98 ± 1.9	900	63 ± 2.5
04	1000	118 ± 1.5	1000	71 ± 1.8

Scanning Electron Microscopy (SEM)

The Surface morphology of 1000 °C sintered HAP powder derived from calcium acetate and calcium nitrate were observed in Fig.5a and 5b respectively. Fig.5a micrograph shows the combination of spherical and

fiber shaped morphology with non uniformed particle size due to the formation of biphasic HAP. Fig.5b reveals that the shape of particles was like ellipsoidal with highly agglomerated. The particle size was in the range of nano to submicron size and this was good agreement with the calculated average crystallite size from scherrer formula.

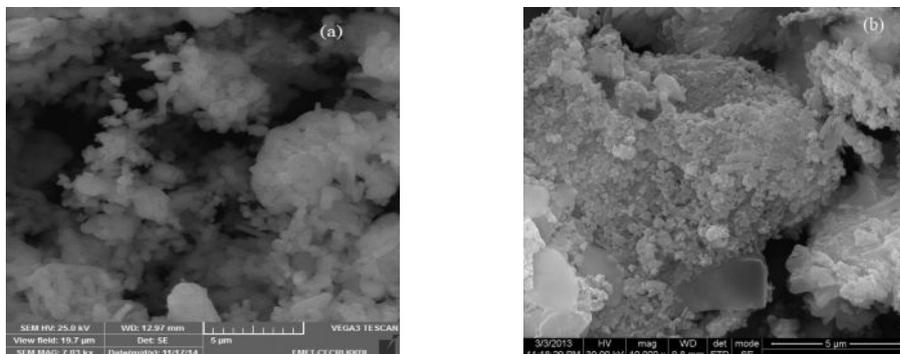


Fig.5. SEM micrographs of (a) Biphasic HAP (b) Pure HAP

Conclusion

In this paper we have synthesized nano HAP at lower temperature by using sol-gel method with two different calcium sources and similar phosphorus material. The XRD analysis confirms the formation pure HAP and biphasic apatite from calcium nitrate and calcium acetate raw materials respectively. The heat treated HAP powder surface morphology and its size was investigated by SEM which confirmed the different morphology of HAP with respect to calcium precursors.

This developed method is simple and affordable for the synthesis of nano HAP with large scale quantity for outstanding applications in dental and orthopedic fields.

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