Synthesis and Characterization of Hydroxyapatite Nanoparticles using Sol-Gel Method

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Abstract

Hydroxyapatite (HAp) is a unique material having high adsorption capacity of heavy metals, high ion exchange capacity, high biological compatibility, low water solubility, high stability under reducing and oxidizing conditions, availability and low cost. Hydroxyapatite nanoparticles have been synthesized by Sol-gel method using Calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$] and Phosphorus pentaoxide (P_2O_5) as starting reactants. The addition of Phosphorus pentaoxide to Calcium nitrate tetrahydrate was carried out slowly with simultaneous stirring. After addition, solution was aged for 10 minutes for maturation. The precipitate was dried at 80°C overnight and further heat treated at 550°C for 2 hours. The dried and calcined particles were characterized by X-ray diffractometry, Fourier transform infra-red spectroscopy and Thermo gravimetric analysis. The particle size and morphology were studied using transmission electron microscopy. TEM examination of the treated powders displayed particles of polygon morphology with dimensions 20-50 nm in length. The FT-IR spectra for sample confirmed the formation of hydroxyapatite.

Introduction

Hydroxyapatite [HAp: $Ca_{10}(PO_4)_6(OH)_2$] is well known as the mineral component of bones and teeth. Thus, it has a considerable interest in dental and medical research [1]. It is the most prominent bioactive ceramics and is widely used and investigated. Applications include coatings of orthopedic and dental implants, maxillofacial surgery and scaffolds for bone growth and as powders in total hip and knee surgery [2-3].

Hydroxyapatite is also an excellent sorption material especially for sorption of heavy metals, It has low water solubility, high stability under reducing and oxidizing conditions. It can be processed with ease and is cost effective [4-7].

Among various technologies used in literature, Chemical synthesis is more prominent. In the present work, hydroxyapatite nanoparticles have been synthesized through sol-gel method because it is a simple and versatile economic route. In the reactions ethanol is used as reaction media. The present work of hydroxyapatite synthesis was focused on the precise control of particle size, morphology and chemical composition.

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Experimental

Materials

Calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$], Phosphorus pentaoxide [P_2O_5], Ethyl alcohol [C_2H_5OH], were used as such without further purification.

Synthesis of Hydroxyapatite

Calcium nitrate tetrahydrate solution and phosphorus pentaoxide solution were prepared by dissolving the desired amounts in Ethyl alcohol at room temperature on magnetic stirrer for 1 hour. Calcium nitrate tetrahydrate solution was added to phosphorus pentaoxide solution drop wise. Slow titration and diluted solutions were used to improve chemical homogeneity and stoichiometry within the system. The resulting solution was aged under continuous stirring for 10 minutes. After aging, the white precipitates obtained were subjected to aqueous washes. The resulting gel was oven-dried in air at 100°C for overnight and calcined in air at 550°C for 2 h (ramp rate = 2°C/min). Figure (1) represents flowchart used for preparation of hydroxyapatite nanoparticles through chemical route.

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Results and Discussion

TGA Studies

Figure 2 shows the TGA and DTGA, thermograms of calcined sample. There are different stages of weight loss during the heating stroke distinguished on the thermograms.

The first weight loss occurs below ~ 200°C corresponding to the dehydration of the precipitating complex and the loss of physically adsorbed water molecules of the HA powder. The second stage of weight loss is between ~ 200°C and ~ 450°C due to loss of lattice water and release of the gases inside the sample. After 550°C the weight loss is due to elimination of carbonate group linked to Hydroxyapatite. It has been noticed that no decomposition of hydroxyapatite is noticed after ~ 750°C.

FT-IR

Hydroxypaptite nanoparticles were analyzed by FTIR. Figure 3 show the FTIR spectra of the sample after calcination. In spectra the absorption due to the vibration modes from phosphates and hydroxyl groups are recorded which represent the HA structure in IR spectra. The bands at 1412 cm^{-1} and 1464 cm^{-1} are attributed to components of the ν_3 mode of a trace amount of CO_3^{2-} , the band at 870 cm^{-1} is attributed to components of the ν_2 mode of CO_3^{2-}, and bands at 1540 cm^{-1} derive from CO_3^{2-} that replace OH^- ions in the HA lattice. Detection of these bands suggest the substitution of PO_4 group in the structure of HA by CO_3^{2-}. The broad peaks at 1650 cm^{-1} and 3200-3350 cm^{-1} show the presence of water.

The bands at 3570 cm^{-1}, and 635 cm^{-1} arise from stretching and libration modes of OH^- ions respectively. The bands at 1102 cm^{-1} and 1054 cm^{-1} arise from ν_3 PO4, the 970 cm^{-1} band arises from ν_1 PO_4, the 601 cm^{-1} and 565 cm^{-1} bands arise from ν_4 PO_4. The group of weak intensity bands in the 2200 cm^{-1} to 1950 cm^{-1} region are derived from overtones and combinations of the ν_3 and ν_1 PO_4 modes.

TEM

Surface morphology of samples were studied by TEM. The micrographs of hydroxyapatite after calcination are shown in Fig 4(A) and 4(B) respectively. These show distribution of

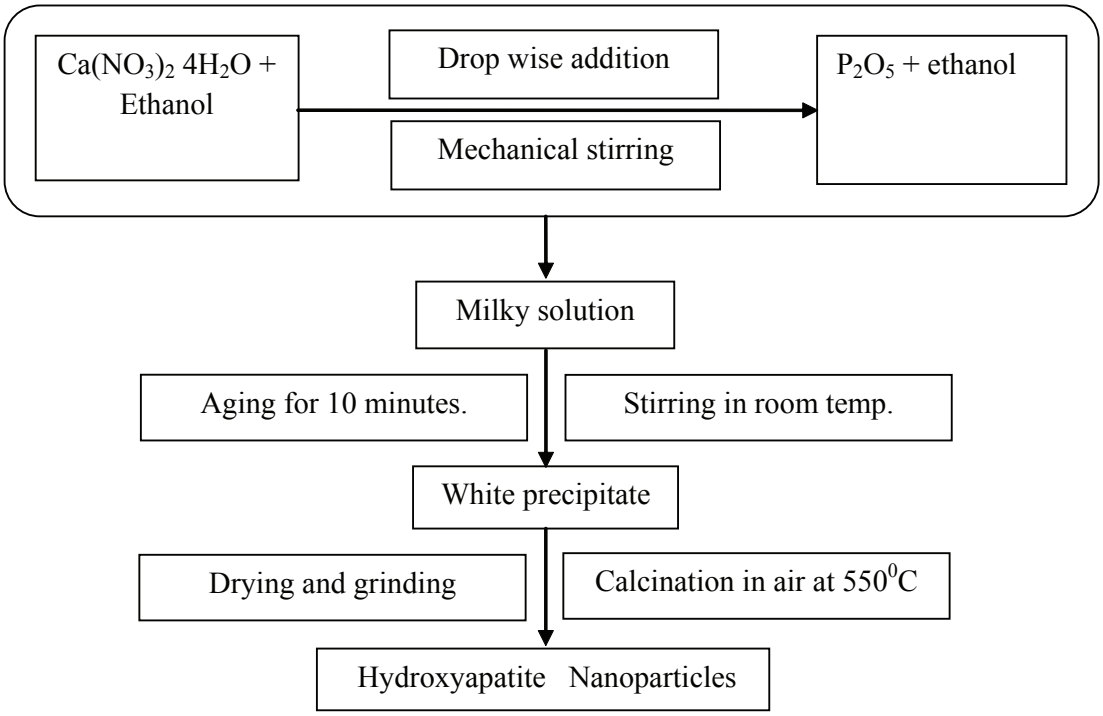

Fig. 1. Flowchart of the Sol-Gel method for Hydroxyapatite nanoparticles

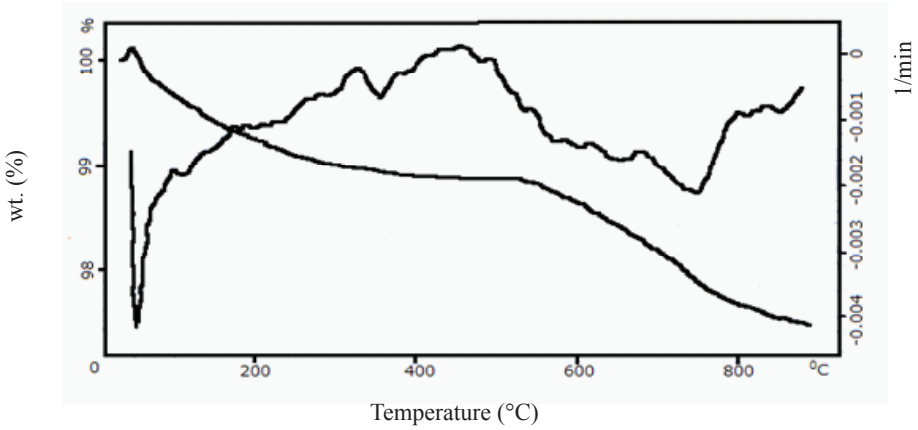

Fig. 2. TGA and DTG for the calcined samples

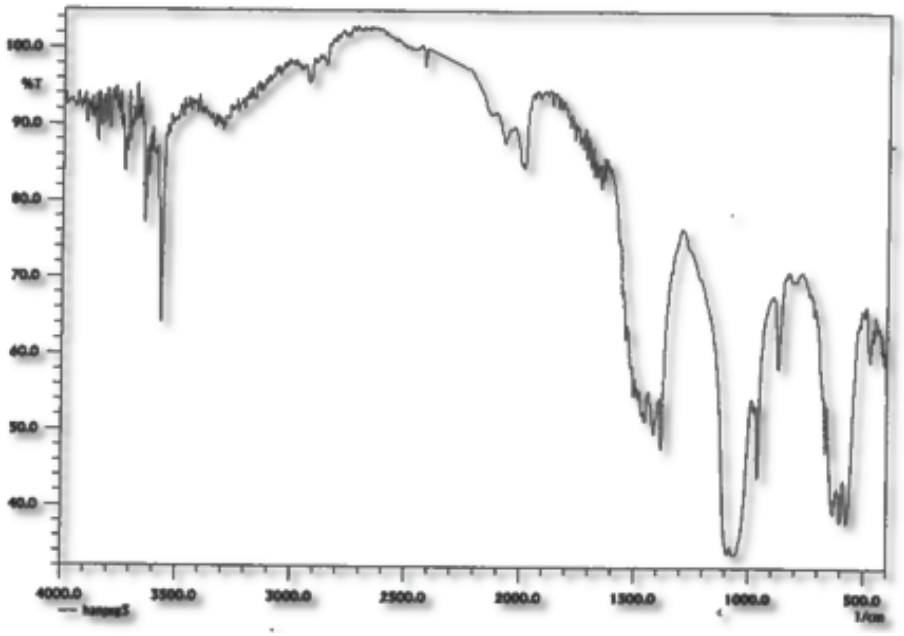

Fig. 3. FTIR spectra for sample after calcination

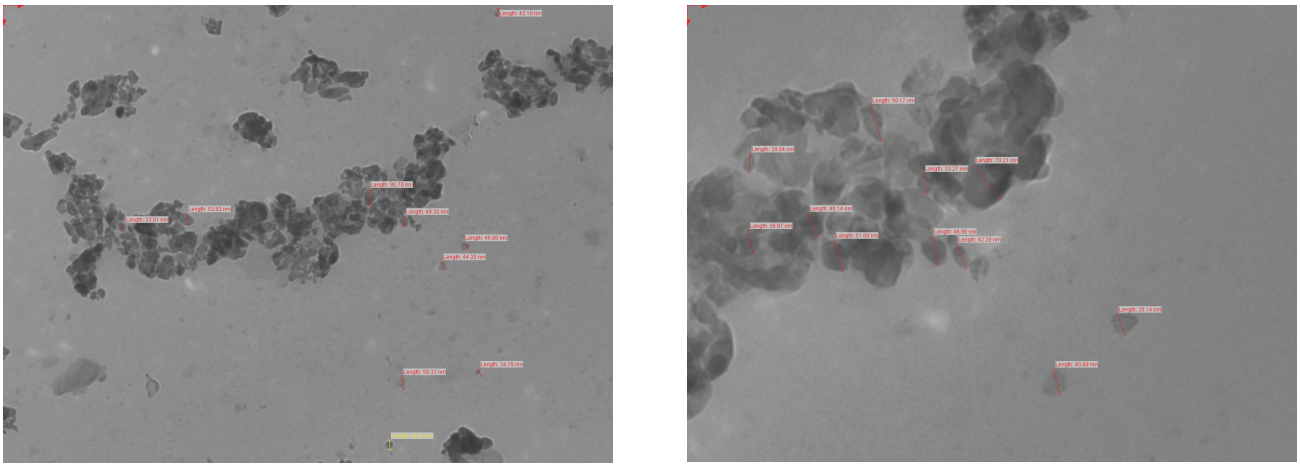

Fig. 4. The TEM images for the Hydroxyapatite nanoparticles Sample

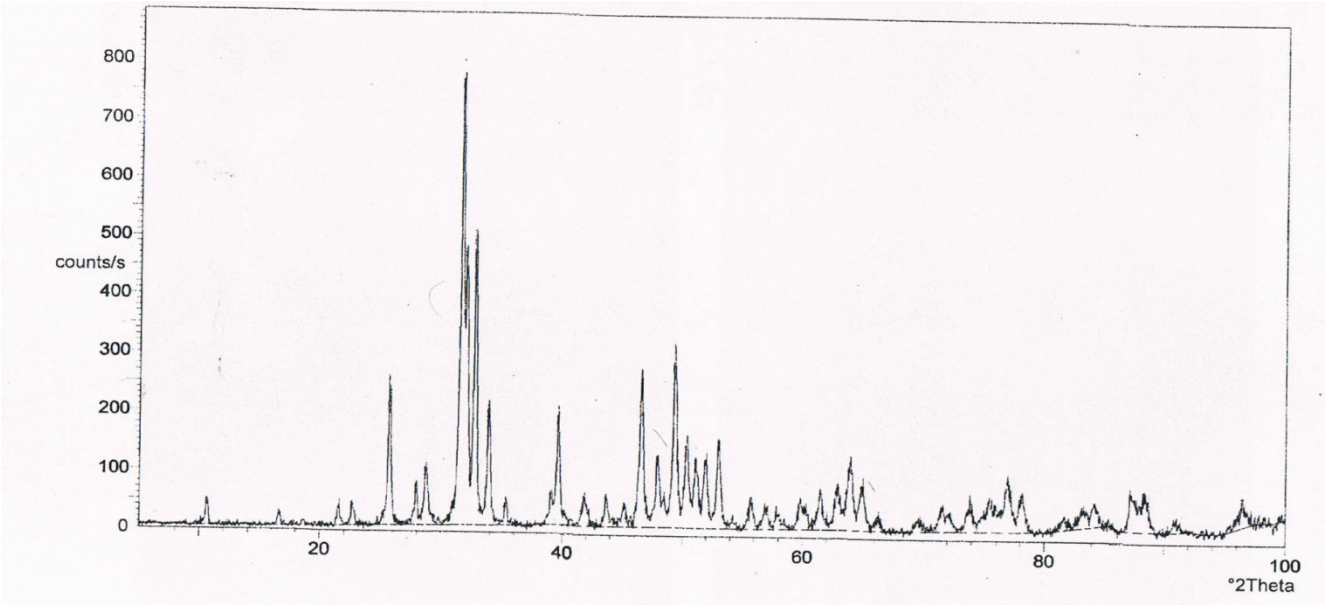

Fig. 5. XRD pattern of Hydroxyapatite nanoparticles after sintering at 550 °C

small particles as well as agglomerates. These agglomerates consist of fine particles that are cold welded together. The particles are mainly composed of Polygon morphology which are 20-50 nm in different directions.

XRD

Figure 5 shows XRD pattern of hydroxyapatite nanopowders after sintering. The straight base line and the sharp peaks of the diffractogram in figure 5 confirms that the product is well crystallized. Peaks observed at 2Θ value of 26.3° and 30.2° as a result of (002) and (120) planes correspond to CaHPO4 phase. Peaks at 28.9° correspond to HA phase. Most prominent peak is at ~31.8 ° corresponding to HA peak (211).

Conclusions

Synthesis of hydroxyapatite nanoparticles was carried out from Calcium nitrate tetrahydrate phosphorus pentaoxide by sol-gel method. The FT-IR and XRD spectra recorded for sample after the calcination confirmed the formation of hydroxyapatite. The basic indication of hydroxyapatite formation are the peaks at around 1102 cm-1,1054 cm-1and 970cm-1 in the IR spectra and XRD peak at 2Θ =31.80. TEM analysis confirmed that particles are mainly composed of polygon nanoparticles with particle size of 20 to 50 nm.

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