Low Temperature Synthesis of Nanocrystalline Hydroxyapatite from Egg Shells by Combustion Method

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Nanocrystalline Hydroxyapatite, which is similar in composition and crystal structure of natural bone, is found to be ideal bone graft substitute due to its controlled resorption in the body fluid upon implantation. This paper reports on a simple combustion technique for synthesizing nanocrystalline hydroxyapatite powder from Eggshell, Diammonium hydrogen phosphate and Citric acid. Fourier - Transform Infrared Spectroscopy and powder X-ray diffraction methods were employed to characterize the sample for phase formation. The particle size is calculated using XRD data, which shows an average diameter of 44 nm. Chemical analyses to determine the Ca:P atomic ratios in synthesized ceramics were performed and it is found to be 1.6.

Introduction

Hydroxyapatite is one of the most versatile material used for implantation purpose due to its similarity to natural bone material. Even though polymer materials play vital role in synthesizing artificial organs, they are neither biocompatible nor bioactive. Hydroxyapatite proves to be highly biocompatible and bioactive but its usage is limited to non-load bearing applications because of its inferior mechanical properties due to poor sinterability. It is possible to rectify this drawback by means of controlling the parameters such as particle size, distribution and morphology.

The eggshell contributes 11% of the total weight of egg. The major constituent present in the shell is CaCO₃, which accounts around 91% of the total weight. India, currently ranks fourth in world in egg production with an annual production of 17,32,500 tons of egg. By taking 11% of the weight, nearly it comes around 1,90,000 tons of eggshell waste is created. This material goes as a waste and leads to pollution since it favours microbial action.

The objective of the present work is to propose an economical way of synthesizing nanocrystalline Hydroxyapatite from eggshell by combustion method.

Experimental Procedure

Uncrushed eggshells were collected and boiled in water for 30 minutes. Then it is placed in hot air oven for 60 minutes to remove the water and moisture content of the shells. Dried shells were crushed to fine powder using laboratory blender. The obtained powder is dissolved in Con. HNO₃, which results in froth formation and the solution turns yellow. The solution formed is allowed to settle down and then its filtered and made-up to known volume. Calcium content of the eggshell solution is determined using EDTA method and it’s found to be 0.25 M.

The standardized eggshell solution is added to citric acid with thorough mixing using magnetic stirrer. The pH value of solution then adjusted to 9.5 by adding 1:1 NH₄OH. 1M (NH₄)₂HPO₄ solution is added to the above mixture at the rate of 1 ml per minute with vigorous stirring. Adding Con. HNO₃ dissolves precipitated HAP and the addition continues until the pH gets adjusted to 1. Resultant solution is stirred until the formation of transparent gel at the temperature of 70°. Gel
formed is kept in a preheated muffle furnace at 250°C and it undergoes combustion with a bright flame. Black coloured precursor obtained is sintered at 900°C for 2 hours, which results in a pure white nanocrystalline Hydroxyapatite.  

Characterization:

Phase purity of the synthesized Hydroxyapatite sample was analyzed in Siemens D-500 X-Ray Diffractometer, using Cu Ka, Ni filtered radiation. The chemical nature and molecular bond structure of the synthesized samples were determined using FTIR (Thermo Nicolet, Avatar 330 FTIR Spectrometer, USA) studies.  

Results and Discussion:

Addition of citric acid to metal ion solution makes the solution viscous with no precipitation or agglomeration of ions from the homogeneous solution. Citric acid is used as a fuel for combustion as well as it forms a polymer matrix, which avoids the precipitation of ions. When the gel undergoes decomposition it forms a fluffy mass which indicates the evolution of CO₂ due to the decomposition of citric acid and the organic constituents of eggshell.

Fig. 1 shows a sharp and well defined XRD patterns for Hydroxyapatite. It is found that HAP is the main phase and the sample got good crystallinity. Absence of peak at 37.36° indicates the absence of free CaO. FTIR spectra of HAP sintered at different temperature and different time duration is shown in fig 2a to 2c. Peaks at 602.2 cm⁻¹, 566.4 cm⁻¹, (60.16 cm⁻¹ and 1044.01 cm⁻¹ indicates the presence of (PO₄)³⁻ groups whereas peaks at 3571 cm⁻¹ and 635 cm⁻¹ shows the presence of OH⁻ group.

The change in concentration of (CO₃)²⁻ ions based on sintering temperature and time duration can be seen from Fig. 2a, Fig. 2b and Fig. 2c where the intensity of the peak corresponding to (CO₃)²⁻ ions decreases. Fig. 2b shows that (CO₃)²⁻ ions substitute in the site of (PO₄)³⁻ and not in the site of OH⁻ otherwise the peak for (CO₃)²⁻ will be observed at1550 cm⁻¹.  

The sample sintered for 2-hour duration shows that the content of (CO₃)²⁻ gets reduced to still lower concentration. Peaks corresponding to pyrophosphate (P₂O₇)⁴⁻, which is highly undesirable, are not seen indicating the absence of it.

The addition of citric acid can also provide a way to synthesize a pure HAP or Carbonated HAP. The substitution of (CO₃)²⁻ for (PO₄)³⁻ groups in HAP cannot be considered as a disadvantage because the natural bone itself
Fig. 1

contains considerable amount of carbonate group in it.

The mean grain size of HAP powder was determined by Debye-Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

Where $D$ represents mean grain size, $\beta$ stands for full width at half maximum of the peak, $\lambda$ is the diffraction wavelength (0.154059 nm), and $\theta$ is the diffraction angle. The mean grain size is 44nm.

**Conclusion:**

Synthesis of HAP starting from eggshells at a low temperature represents a novel way for pro-
Producing a useful bioceramic material. Moreover, combustion method is the apt one for controlling the parameters such as particle size, distribution, and morphology, which will improve the mechanical properties of HAP.

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**References:**