

Synthesis of Hydroxyapatite Bio-Ceramic Powder by Hydrothermal Method

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ABSTRACT

Hydroxyapatite bio-ceramic powder was synthesized using waste eggshells as calcium source by a straight forward thermal method. The process is carried out at high temperature. Different calcium phosphate phases were obtained just by changing the thermal treatment. HAp is the only apatite present in the reaction products, along with minute fractions of other calcium compounds. The final product was characterized by X-ray diffraction, Scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FT-IR). Thermal analysis (TG-DTA) was carried out to investigate the thermal stability of HAp.

Keywords: *Hydroxyapatite, eggshell, X-ray diffraction, FT-IR, TG-DTA*

1. INTRODUCTION

Hydroxyapatite (HAp) is one of the most versatile materials used for implantation purpose due to its similarity to natural bone material [1]. HAp has approximate chemical formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ or $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, and is the main inorganic constituent of bones in humans. Synthetic HAp has been successfully used in hard tissue surgery, as it is capable of undergoing bonding osteogenesis and is relatively insoluble *in vivo* [2]. It is a particularly attractive material for bone and tooth implants since it closely resembles human tooth and bone mineral and has proven to be biologically compatible with these tissues [3-5]. Many studies have indicated that HAp ceramics show no toxicity, inflammatory response, pyrogenetic response. It has excellent fibrous tissue formation between implant and bone, and has the ability to bond directly to the

host bone [3]. Hydroxyapatite (HAp) and other calcium phosphate (CaP) materials exhibit excellent bioactive and osteoconductive properties because of their similarity to natural bone material. HA coating promotes a direct physiochemical bond with bone, which leads to more rapid implant fixation and the development of a stable bone biomaterial interface [6]. Despite the proven ability of HAp to promote bone attachment, long term performance is limited by problems like coating adhesion, rapid dissolution (subsequent loss of bone –bonding), fatigue failure and the creation of particulate debris [7].

Several methods of chemical synthesis have been developed to prepare HAp using various types of Ca and P sources [8-11]. In the present synthesis process, an attempt has been made to synthesize pure and biocompatible HAp powder by using hen's eggshell as the calcium source. The eggshell represents 11% of the total weight of the egg and is composed of calcium carbonate (94%), calcium phosphate (1%), organic matter (4%) and magnesium carbonate (1%).

2. EXPERIMENTAL PROCEDURE

Egg-shells of hen were collected in bulk. They were cleaned mechanically by de-ionized water and boiled in water for 20 minutes. They were then placed in a furnace for a three-stage thermal treatment. Heating rate and soaking time at these three stages are given in Table I. Experimental setup for this synthesis is shown in Fig. 1.

Table I: Three stage thermal treatment of egg-shell

Stage	Temperature $^{\circ}\text{C}$	Heating rate /min	Soaking Time (Hrs)
Stage 1	0-450	7°C	2
Stage 2	450-600	5°C	2
Stage 3	600-900	4°C	1

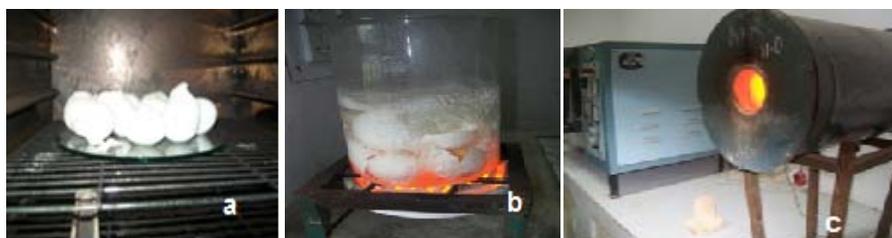


Fig. 1 : Experimental setup for CaO synthesis

In first stage the eggshell heated upto 450°C at the heating rate $7^{\circ}\text{C}/\text{min}$. followed by soaking for two Hrs at 450°C . Similarly in second stage eggshells were heated from $450-600^{\circ}\text{C}$ at heating

rate 5⁰C/min. and soaking at 600⁰C for two Hrs. In final stage the eggshell heated from 600⁰C to 900⁰C at the heating rate of 4⁰C/min followed by soaking for one Hr at 900⁰C.

At the temperature 900⁰C, the eggshells transformed into calcium oxide by releasing carbon dioxide (CO₂) according to the following equation:

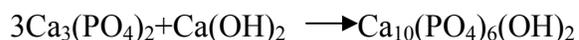


The CaO so obtained from the eggshells was then converted into HAp in a phosphate solution following a procedure reported before by Roy [12], Eric M. Rivera et.al [8] and subsequently used by others [13].

A stoichiometric amount of calcined eggshell was dispersed in well-degassed distilled water. Under vigorous stirring reagent grade tri-calcium phosphate solution (Merck) was mixed into calcined eggshell solution at a controlled into the suspension maintained at 90⁰C temperature. Mixing was continued for more time to achieve proper mixed solution. After completion of mixing, the solution was subjected to aging treatment for 24 Hrs and then filtered. The filtered solution was further heat treated in presence of steam atmosphere. The rate of heating was 15⁰C/min. up to 650⁰C, 8⁰C/min from 650⁰C to 900⁰C followed by soaking for 1 Hrs at 900⁰C. Steam is supplied to maintain H₂O presence during reaction. The expected reaction is given as:



As the synthesized powder obtained from eggshell contain few parts of calcium hydroxide along with calcium oxide so other probable reaction is



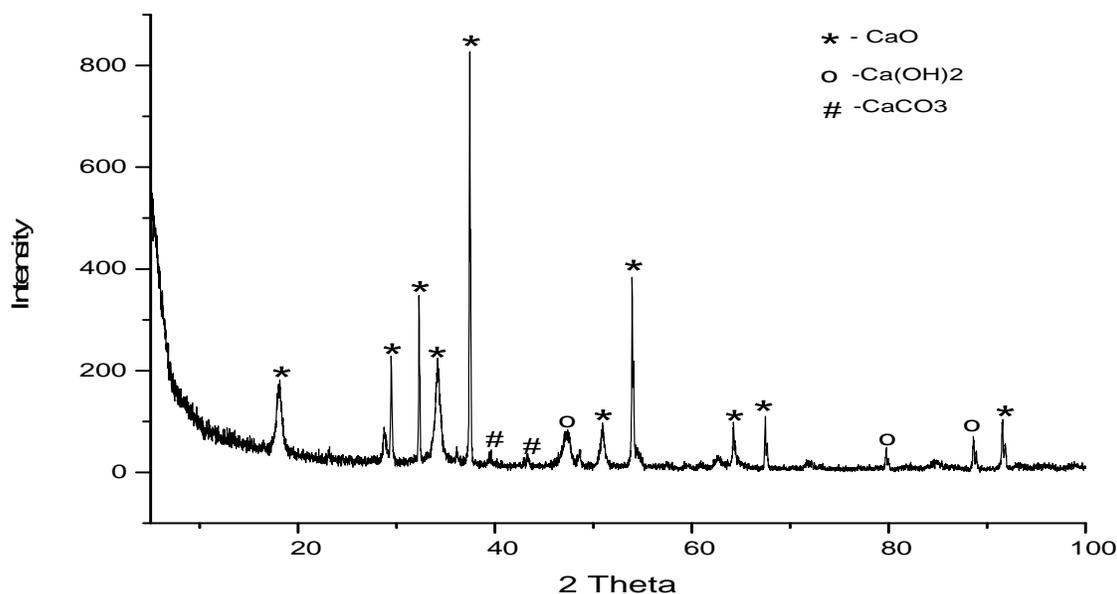


Fig. 2: The XRD of Calcium oxide (CaO) produced from Egg Shell

2.1 Characterization of the Product

X-ray diffraction analysis of the product in Fig. 2 shows intensity peaks corresponding to JCPDS 37-1497 files for CaO, with some fraction of other species $\text{Ca}(\text{OH})_2$, CaCO_3 . The observed change in the weight corresponds to loss of gaseous CO_2 .

The X-ray powder diffraction (XRD) analysis of the synthesized HAp samples was done (Bruker D-8 Advanced, Germany) in reflection mode with $\text{Cu K}\alpha$ ($\lambda=1.5405 \text{ \AA}$) radiation. The data were analyzed in the 2θ range from 10° to 80° with a scanning step of 2° per min. The results reveal that the thermal processing of CaO in the phosphate solution at 950°C produces a solid material of white color with porous structure having pores of irregular diameter and high mechanical strength. X-ray diffraction of this sample in Fig. 3 shows several phases. The crystalline phases was identified as HAp (JCPDS, 9-0432), with some phases of calcium oxide (JCPD, 37-1497). and calcium hydroxide (JCPDS,4-0733). These phases may be attributed to incomplete transformation of calcite, resulting from interruption in supply of steam atmosphere at the high temperature during reaction process.

The functional groups present in HAp were ascertained by Fourier transform infrared spectroscopy (FT-IR) Thermo NICOLET 5700, FTIR. The FT-IR spectra were obtained over the region $400\text{--}4,000 \text{ cm}^{-1}$ using KBr pellet technique with spectral resolution of 4 cm^{-1} .

The TG–DTA analysis was done with An Perkin Elmer (Pyris Diamond) thermal analyzer. The weight loss and thermal stability of the samples were also evaluated from the thermo gravimetric analysis data. The heating rate of $10^{\circ}\text{C}/\text{min}$ was employed upto temperature 1400°C in air atmosphere

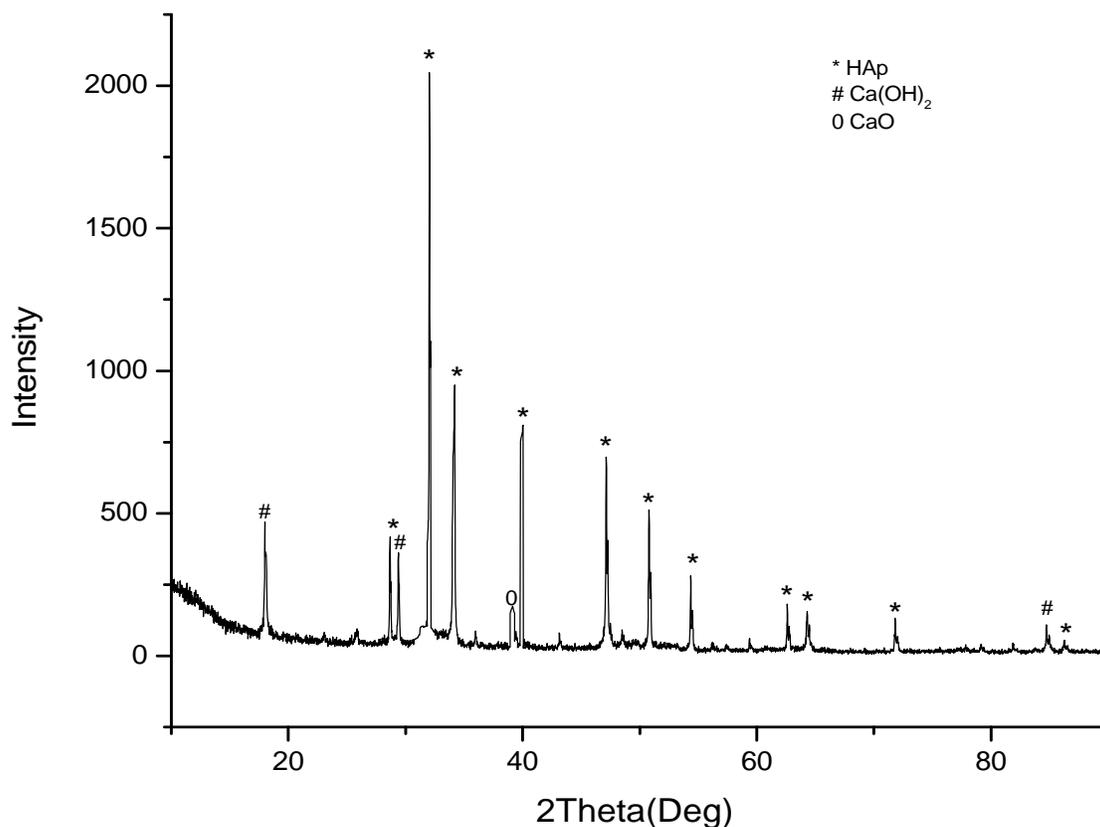


Fig. 3: The XRD of synthesized HA

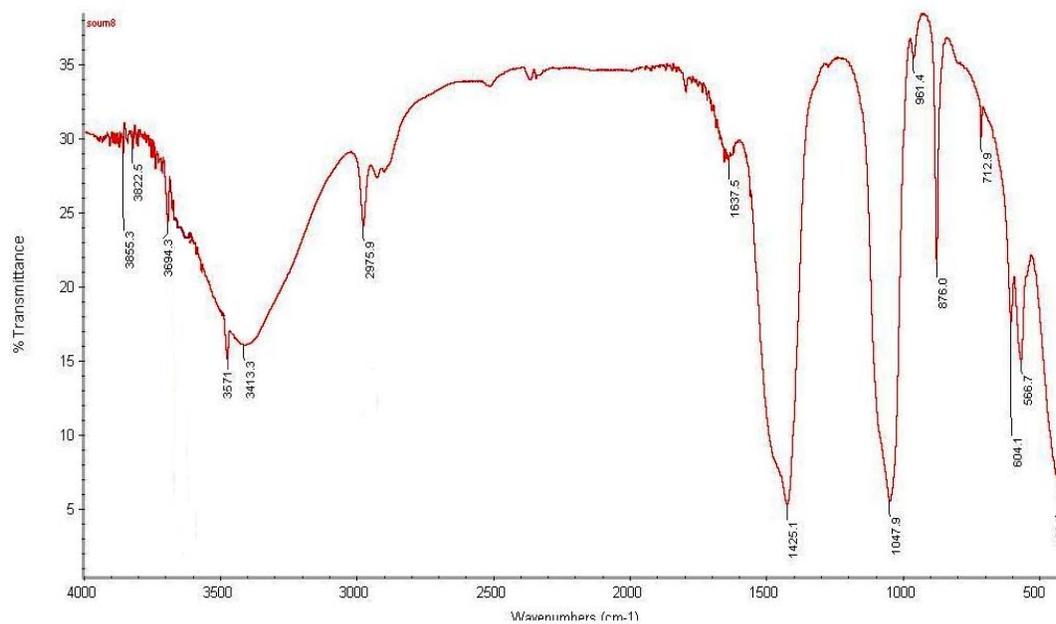


Fig.4: FT-IR spectrum of synthesized HAp

3. RESULTS AND DISCUSSION

The FT-IR spectrum of the HAp produced by hydrothermal method shown in Fig.4 shows all the characteristic bands for Hydroxyapatite [14, 15]. The asymmetric stretching (ν_3) and bending (ν_4) modes of PO_4^{3-} ion were detected at around 1047.9, and 604.1 and 566.7 cm^{-1} , respectively. The symmetrical stretching modes (ν_1 and ν_2) of PO_4^{3-} ion were also found at around 961.4 and 470.4 cm^{-1} , respectively.

The liberation and stretching mode of the OH^- were detected at around 3571 and 1637 cm^{-1} , respectively. The stretching vibrations, ascribed to CO_3^{2-} at around 1425.1, and 876 cm^{-1} were also present [16]. The bands at 3413.3 and 1637.5 cm^{-1} correspond to adsorbed H_2O .

XRD patterns of HAp shown in the Fig.3, shows a broad reflection peak in the range of 31.8-32.5 $^\circ$ of 2θ values, which corresponds to the characteristic peak of apatite phase (according to JCPDS card # 9-432).

Analysis of the SEM micrographs presented in Fig. 6 shows that the synthesized HAp consisted of agglomerates. The shapes of which were almost the same and the size was always between 3 μm and 5 μm , built up from fine particles about 400 nm in size. Individual fine particles with spherical and semi-spherical shapes were observed as seen in Figure (6a). The agglomerates

(Fig: 6b and 6c) were of irregular shape like oval shape and spherical shape. Agglomerates as big as $10\mu\text{m}$ could also be seen, however, the dominant sizes were between 3 and $5\mu\text{m}$. There are many spherical agglomerations and crystallites of nano-sized with a tendency to agglomerates leaving pores in between. The formations of pores are beneficial as they would permit the circulation of body fluid throughout the coating when it is used as biomaterial.

DTA-TG (Fig.5) analysis shows that there is weight loss of around 6% upto temperature 380°C and 10% in the range 380°C to 420°C . This major loss confirmed the formation of HAP, similarly about 9% wt. loss was observed upto 800°C . Beyond 800°C to 1400°C no significant wt. loss was observed. Almost stable curve was noticed within this temperature range, which indicates thermal stability of HAp powder.

The result shows thermal stability of HAP beyond the temperature 1050°C as proposed [17]. In DTA curve there is indication of endothermic sharp peak at 420°C with two other small peaks.

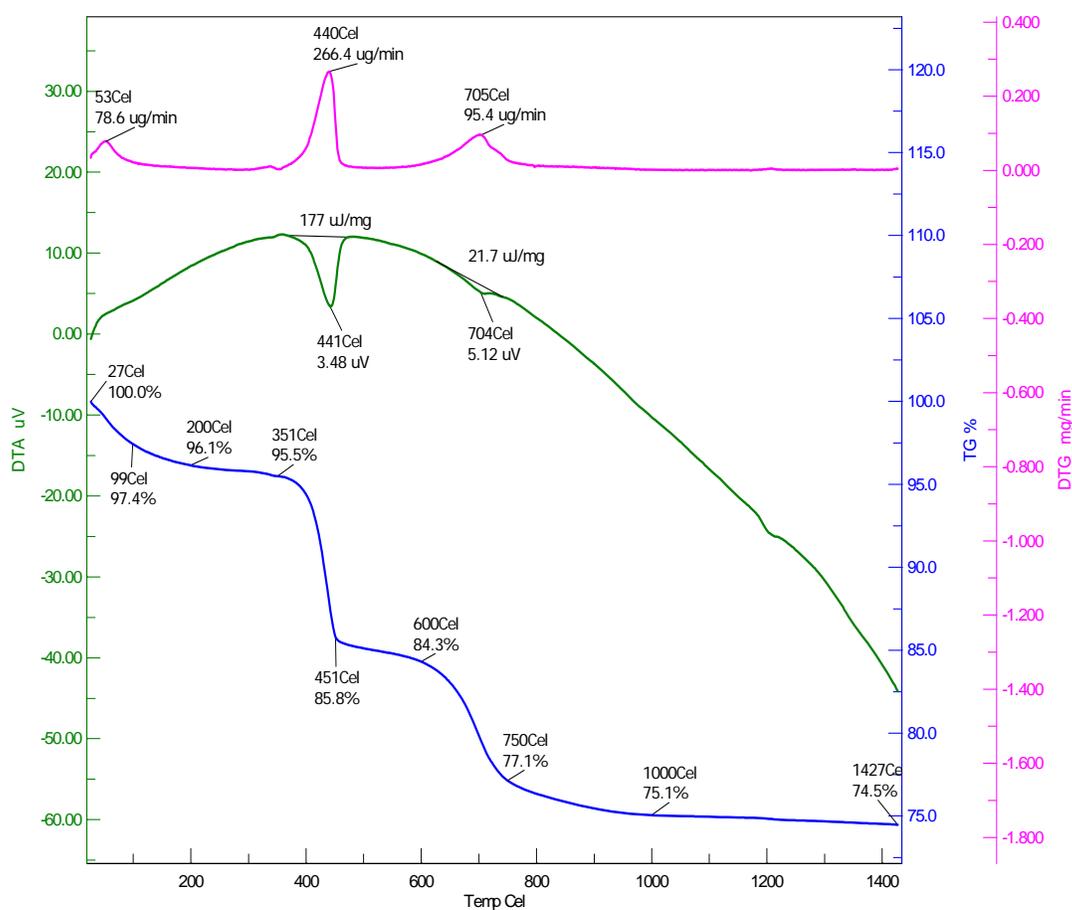


Fig.5: DTA-TG analysis of synthesized HAP.

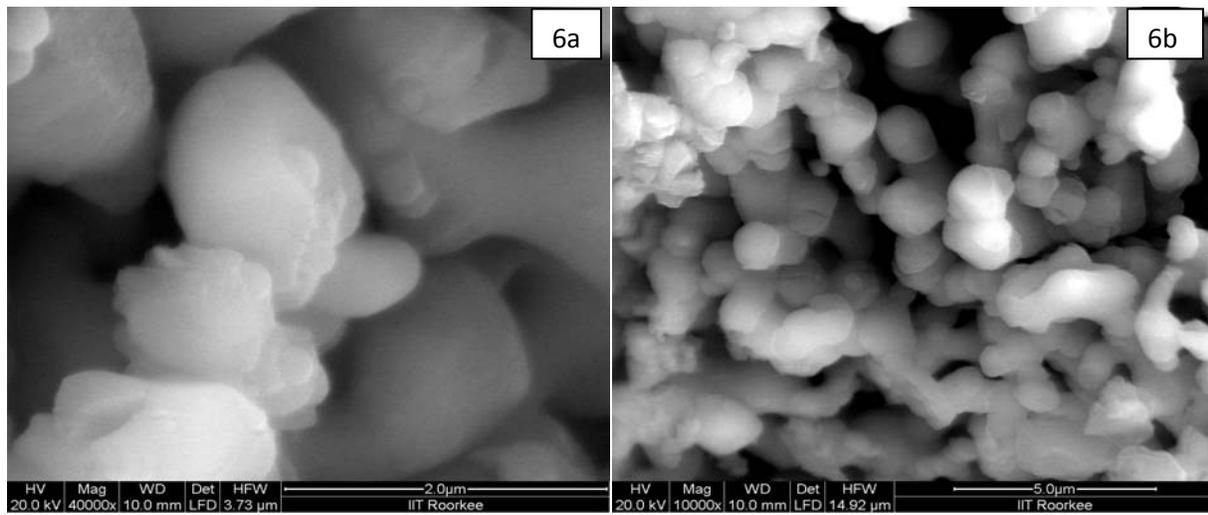


Fig. 6a & 6b: SEM micrographs of synthesized HAP

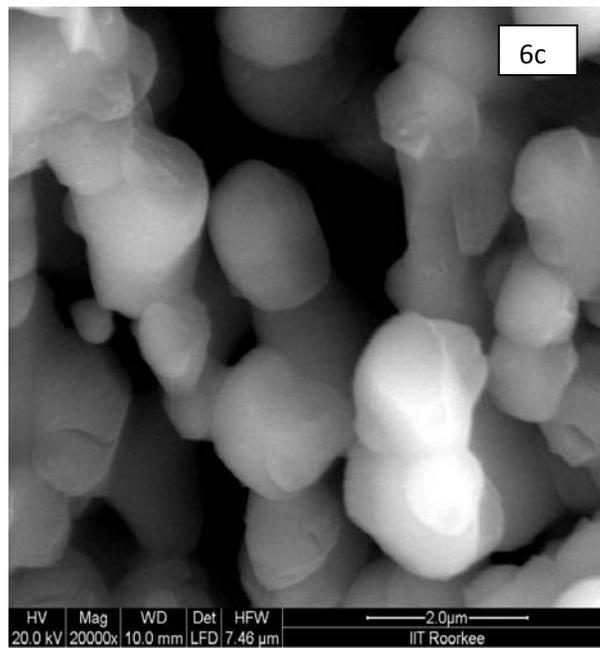


Fig.6c: SEM micrographs of synthesized HAP

4. CONCLUSION

HAp has been successfully synthesized by reaction of discarded hen eggshell with tri-calcium phosphate in presence of steam at 900°C and subsequent aging for 24 Hrs results in formation of synthesized HAp. As revealed by FT-IR and XRD analyses, the product is crystalline & DTA-TG shows good thermal stability. The particles are mostly spherical with nano-size. This method requires only low temperature treatment (900°C) as compared to conventional method where temperature of treatment is 1050°C.

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