A Convenient Synthesis Route of Hydroxyapatite from Egg Shells

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Abstract

Hydroxyapatite is well known bioceramic that possess excellent in-vivo and in-vitro properties due its chemical and structural similarity with mineral part of bone and is widely used as bone graftmaterial in orthopedic surgery and dental implants. In this research a simple green chemistry and environment friendly wet precipitation rout was adopted for synthesis of micro crystalline hydroxyapatite from egg shells by using phosphoric acid as phosphorus precursor. Resulting powder was characterized using TGA/DTA for thermal stability, XRD for structural analysis which proved phase purity andSEM for morphological evaluation which showed spherical particles. FTIR and particle size analysis was also performed.

Introduction

Egg shell demonstrate a multilayered structure, outermost layer is called cuticle and then comes the spongeous layer then lamellar layer. It is the spongeous and lamellar layer that makes the matrix of egg shell's structure. This matrix is constituted of protein fibers bonded to calcite crystals in a ratio of 1 to 50 [1]. Strength of egg shells is attributed to the fact that calcite particles are not only surrounded by protein fibers but these fibers also pass through the crystals. Egg shell is 11% by weight of its egg and is composed of calcium carbonate (94%), calcium phosphate (1%), organic matter (4%) and Magnesium carbonate (1%) [2]. A large amount of egg shells is produced every year and their shells as a waste contribute to environmental pollution. According to a survey Pakistan produces 1.1 Million eggs each year and taking average weight of 746 grams for one dozen[1] the net weight of shells is about 75000 tons per year. This waste of egg shells leads to pollution because it favors microbial action.

Scientists have spent years to use calcium phosphate based minerals as bone replacement materials[3]. Hydroxyapatite (HA) is calcium phosphate based ceramic material which is similar to natural bone in its crystal structure and stoichiometry [4-6]. HA has capability to form direct chemical bonds with surrounding tissues which makes it bioactive and biocompatible [7]. HA is not well suited for wet environments [8] so it is not used in load bearing applications in physiological conditions but is commonly used as coating material for metallic implants [9].

A paradigm shift in chemistry has occurred since publication of survey report of commission on physical sciences by national research councilin Washington DC [10]. ''Green Chemistry is the use of chemistry techniques and methodologies that reduce or eliminate the use or generation of feedstocks, products, by-products,solvents, reagents, etc. that are hazardous to human health or the environment'' [11]. We can further include the term use of hazardous products/waste to make environment friendly and valuable products. Briefly speaking it is the chemistry for pollution inhibition. In current research authors have developed a green chemistry and environment friendly rout for synthesis of Hydroxyapatite from egg shells.

Experimental Procedure

Washed and dried egg shells were ground in mortar and pestle and resulting powder was heat treated at 250°C for one hour and then at 1000°C for three hoursresulting in calcium oxide powder. 0.5M solution of calcium oxide was prepared whoseinitial pH was at 13-14. Then 0.3M phosphoric acid was added to it drop wise at droppingrate of 30-40 drops per minute. The solution was then refluxed at 80°C for 3 hours keeping $p_H$at 10 and after that it was stirred for 20 hours. Then precipitates were filtered, washeduntil pH of filtrate become 7 and then dried in hot air oven at 80°C for twelve hours. A few gram of resulting powder was heat treated at 900°C for one hour.

Characterization

STOE Diffractometer with CuKa was used for X-ray diffraction analysis in the scan range of 20° to 80° with step size of 0.04°. JEOL JSM 6490A was used for morphological and microstructural studies. FTIR analysis was performed between scan ranges of 400cm^{-1} to 4000cm^{-1} by Perkin Elmer FTIR. And thermal gravimetric studies were performed by Perkin Elmer TG/DTA for temperature range of room temperature to 900°C with heating rate of 10°C per minute.

Results and Discussion

XRD Analysis

Figure 1(a) shows the diffraction plot of powder washed egg shells which is perfectly matching with Calcium Carbonate (JCPDS 01-085-1108) which is in confirmation with the literature as stated earlier. When this egg powder is heat treated at 1000°C then calcium carbonate decomposes to give calcium oxide (Figure 1 (b). after heat treatment we left with only mineral phase which is purely calcium oxide, confirmed by matching with JCPDS 00-

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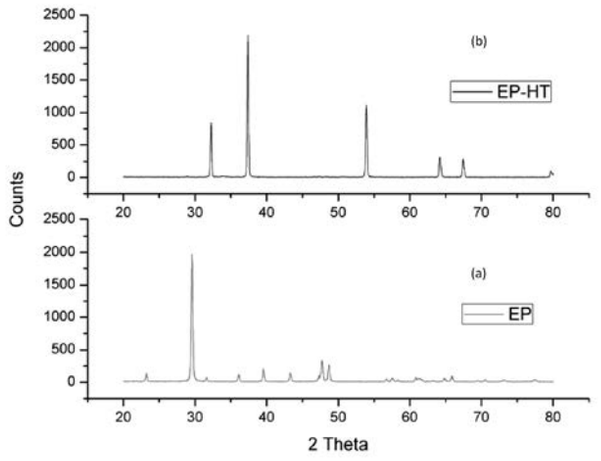

Fig 1.(a) XRD pattern of washed egg powder (Ep), (b) XRD plot of heat treated egg powder (EP-HT).

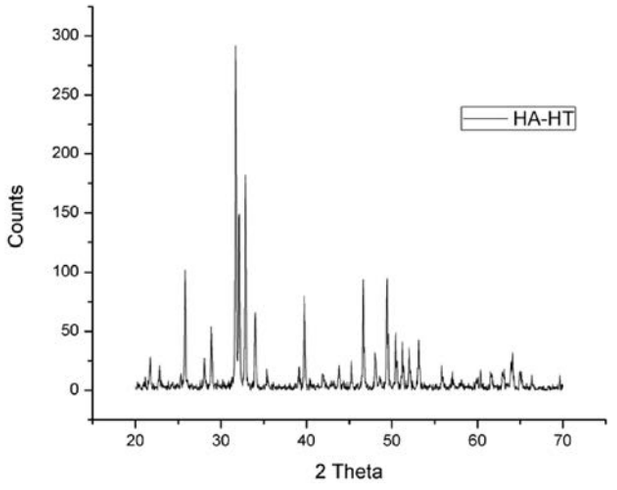

Fig. 2. X-Ray Diffraction pattern of synthesized Hydroxyapatite after heat treatment at 900°C.

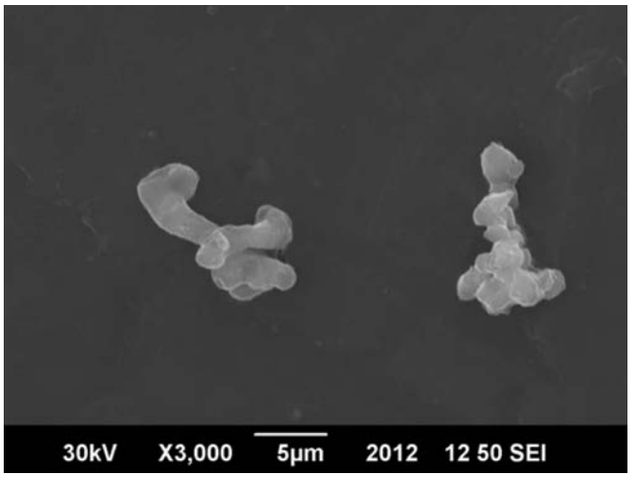

Fig. 4.SEM Image of calcined (at 900°C) egg shell powder.

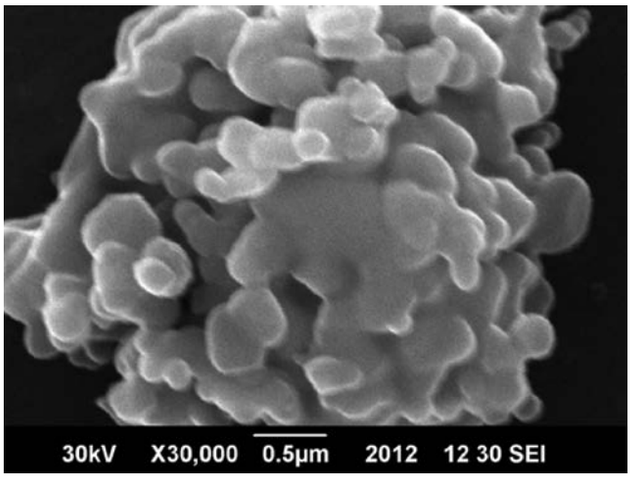

Fig. 5. SEM micrograph of synthesized Hydroxyapatite after heat treatment at 900°C.

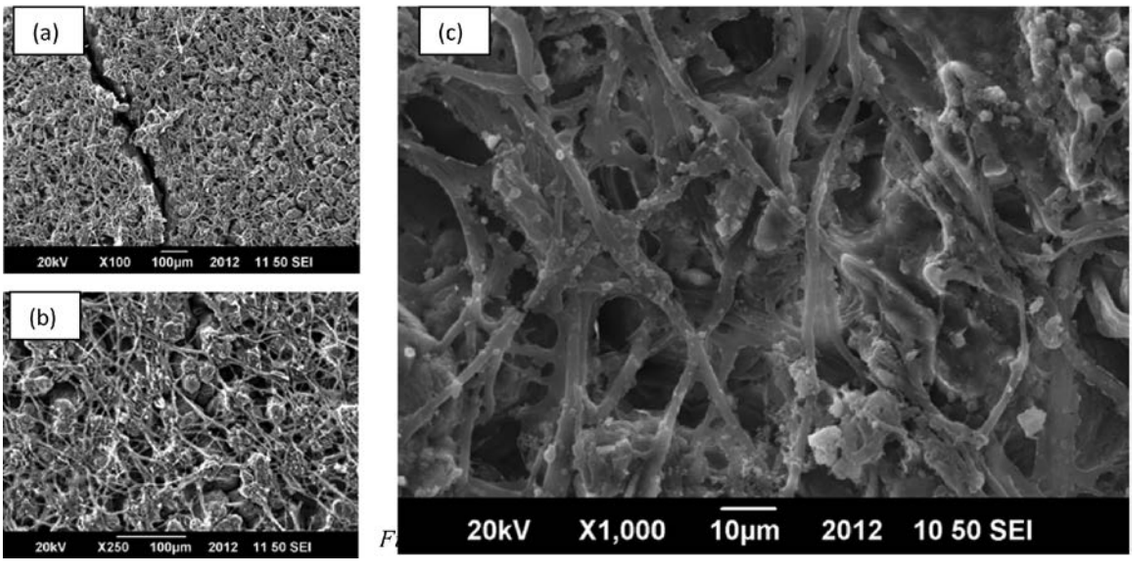

Fig. 3. SEM images of Internal face of egg shell.

Table 1: EDS analysis of Egg powders

Element	Egg Powder		Calcined Egg Powder	
	Mass %	Atomic %	Mass %	Atomic %
Ca	12.75	19.30	67.37	45.73
O	60.29	68.48	32.63	54.27
C	26.95	12.22	--	--

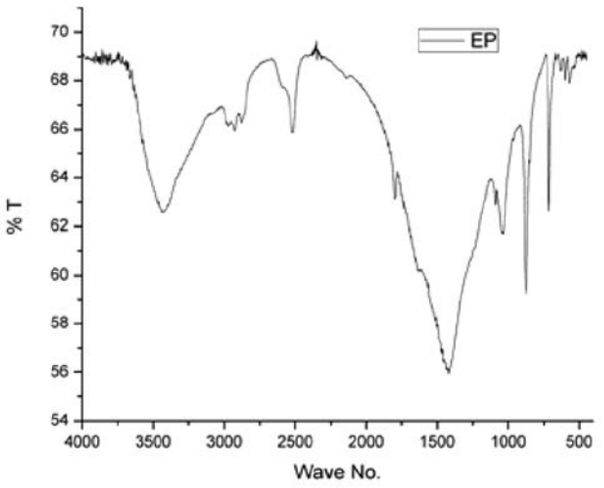

Fig 6. FTIR spectrum of egg shell powder.

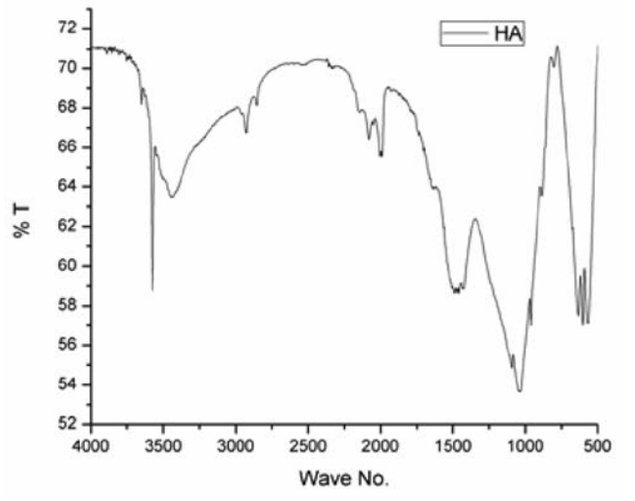

Fig 7. FTIR transmission spectrum of synthesized Hydroxyapatite.

048-1467. The high temperature decomposition can be demonstrated by equation 1. The carbon dioxide gas produced gets ejected out of powder leaving behind the calcium oxide.

$$CaCO_3 \longrightarrow CaO + CO_2 \quad (1)$$

After reaction with phosphoric acid a phase pure hydroxyapatite forms as depicted from XRD plot of resulting product powder as it perfectly matches with JCPDS 009-0432, shown in figure 2. Presence of no other phase indicates that HA was the only stable calcium phosphate phase in that synthesis conditions.

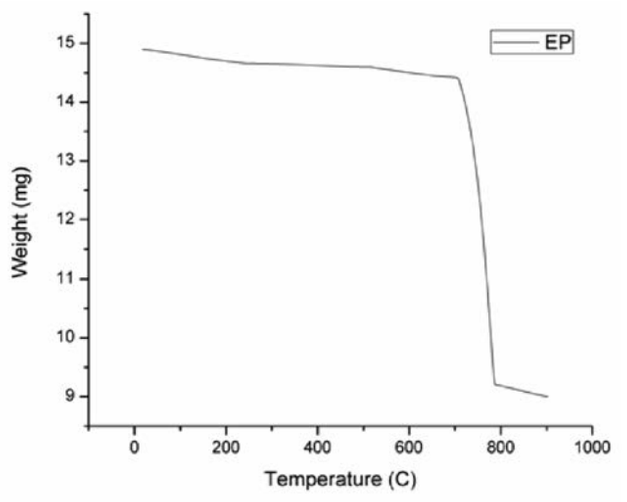

Fig 8.TGA plot of egg powder.

SEM Analysis

Internal surface of cleaned and washed egg shell is shown in figure 3. It is clearly evident that organic matrix makes the continuous entangled network holding mineral phase in its entanglements. The organic fibers are not only surrounding the mineral crystals but also passing through these giving strength to the structure.

Figure 3 (a-c) is showing the SEM micrograph of crushed egg powder dried at 250°C while Figure 4 is showing SEM image of calcined egg shell powder. EDS results of these powders are shown in Table 1 and it is clearly evident that it is Ca, O and C comprising the dried egg shells which is confirmation of XRD results. While it is only the Calcium and Oxygen in the calcined egg shell indicting it is purely calcium oxide.

Figure 5 is SEM image of resulting hydroxyapatite after heat treatment at 900°C. Particle size is ranging from 200nm to 500nm with almost spherical to capsule like morphology.

FTIR Analysis

FTIR transmission spectrum of egg shell powder is shown in figure 6 taken at room temperature. The results are matching with earlier research on egg shells [12]. The absorption peaks at 700cm^{-1}, 879cm^{-1} and 1415cm^{-1} are corresponding to υ_4, υ_2 and υ_3 vibration modes of Co_3^{-2} respectively, whereas υ_2 is out of plane bend mode, υ_3 is asymmetric stretching mode and υ_4 is the in plane vibration mode.The broad absorption band at 3400cm^{-1} is due to stretching vibration of molecules of structural water. The absorption peaks in the regime of 2500cm^{-1} to 3000cm^{-1} are due to organic contents/

FTIR results of synthesized hydrooxyapatite are shown in figure 6 which is in agreement with the

characteristic spectrum of crystalline HA. Peaks at 577cm^{-1} and 607cm^{-1} are corresponding to bending modes of O-P-O bonds while the peak at 642cm^{-1} is of vibration mode of hydroxyl group. It is also important to note that sharpness of bands at these wave numbers indicates that the Hydroxyapatite is crystalline in nature. P-O symmetric stretching gives absorption peak at 987cm^{-1} and it is asymmetric stretching of P-O bond that is showing peaks at 1112cm^{-1} and 1061cm^{-1}. OH stretching mode is showing its characteristic peak at 3576cm^{-1}.

Thermo gravimetric analysis (TGA)

TGA plot of egg shell powder from room temperature to 900°C is shown in figure 8. It is clear that losses are slow till 650°C and these small losses are may be due to loss of structural water and decomposition of organic matter.While at temperatures above 650°Cmajor weight losses of about 37% occurred and these losses are primarily due to loss of CO_2 during decomposition of egg shell carbonaceous matter to form calcium oxide as given in equation 1.

Conclusions

Phase pure hydroxyapatite is successfully synthesized from egg shell powder after heat treatment and simple reaction with phosphoric acid.This is an environment friendly and low cost rout to produce a valuable product. HA particles ranging in size from 200nm to 500nm are obtained.

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