Microwave irradiation synthesis of 3D flower-like hydroxyapatite

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Abstract— Microwave synthesis of Hydroxyapatite (HA) using three different calcium precursors and EDTA as organic modifier has been reported in this paper. Scanning electron microscopic and X-ray powder diffraction studies revealed the formation of self assembled 3D hierarchical flower-like HA with some influence of the precursor used.

Index Terms— Biowaste, EDTA, Egg shell, Flower-like, Hydroxyapatite, Microwave irradiation,.

1 Introduction

IN the recent past contrary to agglomerates hierarchical nanostructure have attracted much attention due to the high surface area, enhanced properties etc [1],[2]. Hydroxyapatite (HA) is an important inorganic biomaterial which is being investigated for more than four decades [3]. Various methods such as hydrothermal, sol-gel, wet precipitation, microemulsion, microwave irradiation etc are available for the synthesis of HA [4]. Among these methods microwave irradiation synthesis has several advantages like fast reaction, high yield, purity, energy and time saving process hence it is a method suitable for fast extraction of samples [5]. HA can be derived from various natural sources such as corals, fishbone, eggshell, snail shells etc [6],[7],[8]. Recently we started working on the synthesis of HA from eggshell biowaste which is a economic resource. As a part of the work comparison has been made between the HA prepared from commercial calcium precursors such as calcium nitrate and calcium carbonate with the HA prepared using eggshell as the calcium precursor. Here we report the micro morphological details of the HA obtained from the three different precursors.

2 Experimental

All the chemicals used for the experiments were analytical grade obtained from Merck, India. CaCO3 was extracted from eggshell after thorough cleaning and removing organic components by sodium hypochlorite solution. 14g of Ca(NO3)2.4H2O was then mixed with 0.14M of EDTA solution to form Ca-EDTA complex. Subsequently, 0.08M of Na2HPO4 solution was slowly added with the obtained Ca-EDTA complex while maintaining the pH at 13 using NaOH solution and stirred for 30 min. Then, the prepared reaction mixture was kept in a microwave oven (2.45 GHz, 600 W, LG, India) and irradiated with microwave for 3 hours. The white product formed was washed three times using distilled water and dried at 110°C in hot air oven for 5 hours it was designated as HA1. For comparison instead of Ca(NO3)2.4H2O eggshell powder and commercial CaCO3 were used as the calcium precursors in the above procedure and the powders obtained were named as HA2 and HA3.

The powder X-ray diffraction (PXRD) patterns of the as-synthesized samples were recorded using a Rigaku MiniFlex II powder X-ray diffractometer in the range between $20^\circ \leq 2\theta \leq 60^\circ$ with Cu Kα monochromatic radiation (1.5406 Å). The average crystallite size was calculated from PXRD data using the Scherrer approximation

$D_{hkl} = K\lambda/\beta\cos\theta$ and the degree of crystallinity (Xc) was evaluated using $Xc = (0.24/\beta 002)3$ where K is the broadening constant chosen as 0.9, λ is the wavelength of Cu Kα radiation (1.5406 Å), θ is the diffraction angle (degree) and β002 is the full width at half maximum (degree) of (002) Miller's plane. The morphology of the as-synthesized samples was examined using a Zeiss ultra plus scanning electron microscope (SEM).

3 Results and Discussion

Microstructural observation by SEM revealed self assembled 3D hierarchical flower - like structure for all the samples (Fig.1) but close observation of the structure showed distinct differences. Each flower like structure is made of large number of nanosized individual leaf like crystals of 200–500 nm width and 1-2 μm length that are extending radially from a center. Individual crystals of HA1 and HA3 synthesized using the commercial precursors are distinct with smooth surfaces and hexagonal facets while in HA2 many individual leaflets are fused together and the facets are not much obvious.

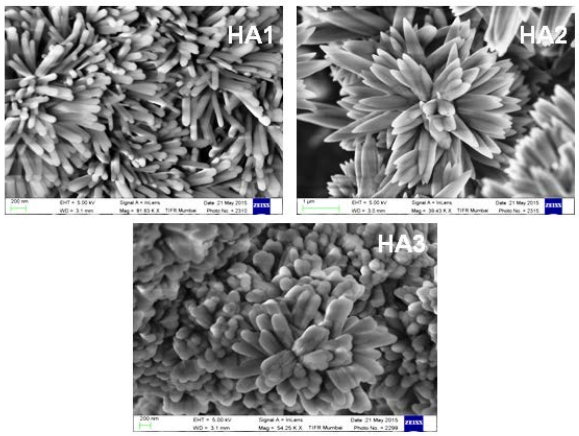

Fig. 1. Microstructure of samples HA1, HA2 and HA3

This may be attributed to the purity of the commercial precursors and the trace elements present in the precursor derived from eggshell. At pH 13 Ca-EDTA complex acts as a highly stable hexadentate unit offering equal probability for the anisotropic growth of crystals along the c-axis leading to the formation of flower - like structures [9].

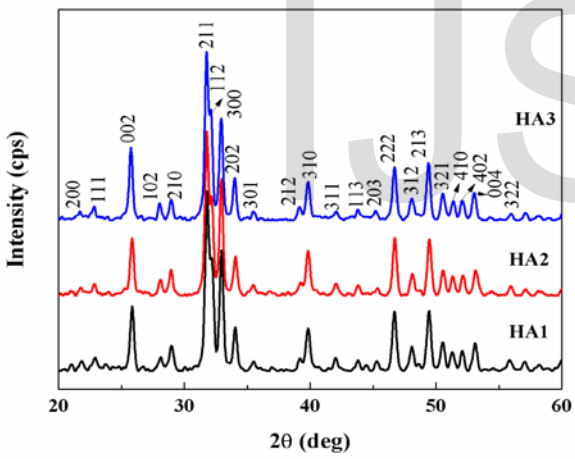

Fig. 2. XRD pattern of HA1, HA2 and HA3 samples

XRD patterns (Fig 2) obtained for the three samples exhibited the emergence of diffraction peaks in striking similarity to that of HA belonging to JCPDS File No: 09-0432. XRD patterns did not exhibit any significant differences though the precursors choosen were different. The peaks in the region 30-35° can be ascribed to the characteristic (211), (112), (300) and (202) reflections of HAp. The calculated average crystallite size and the degree of crystallinity are 3.9518, 4.9949 & 6.1909 and 55, 59 & 62 nm respectively

4 Conclusion

Microwave synthesis of HA using EDTA as organic modifier has resulted in the formation of self assembled 3D hierarchical flower like HA. The precursor used for the synthesis showed some influence on the flower like structure.

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