OLIVE OIL ASSISTED SYNTHESIS OF NANO HYDROXYAPATITE BY HYDROTHERMAL METHOD

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ABSTRACT *Hydroxyapatite is a bioceramic material, which is widely used in various biomedical applications, mainly in orthopedics and dentistry due to its close similarities with inorganic mineral component of bone and teeth. Synthetic hydroxyapatite is known to be similar to the one obtained naturally in terms of the crystallographic structure and chemical composition. Hydroxyapatite nanopowders were synthesized using calcium nitrate and ammonium dihydrogen phosphate as calcium and phosphorous precursors, respectively and olive oil as an additive by hydrothermal method. The presence of phosphate functional groups in the Fourier transform infrared spectra suggest the formation of hydroxyapatite. The powder X-ray diffraction analysis confirms the formation of single phase hydroxyapatite and an increase in crystallinity of hydroxyapatite synthesized with the addition of olive oil. A change in shape from spherical to rod-shaped particles is observed for hydroxyapatite synthesized with the addition of olive oil.*

Keywords: *Hydroxyapatite, hydrothermal synthesis, olive oil*

1. Introduction

Hydroxyapatite (HAp) with the chemical formula [$Ca_{10}(PO_4)_6(OH)_2$] has been extensively used in medicine for implant fabrication owing to its similarity with mineral constituents found in hard tissue (i.e. teeth and bones) [1,2]. Because of its high level of biocompatibility, it is commonly the material of choice for fabrication of dense and porous bioceramics [3]. Unfortunately, due to low mechanical reliability, especially in aqueous environments [4]. HAp bioceramics cannot be used for heavy load-bearing applications. Thus, its general usage includes biocompatible phase reinforcement in composites, coatings on metal implants and granular fill for direct incorporation into human tissues [1-3]. Non-medical applications of HAp include packing media for column chromatography, gas sensors, catalysts and host material for lasers [5]. Properties of HAp, including bioactivity, biocompatibility, solubility, sinterability, castability, fracture toughness and adsorption can be tailored over wide ranges by control of particle composition (e.g. lattice substitution), particle size and morphology [1-3, 6]. For these reasons, it is of great importance to develop inexpensive HAp synthesis methods focused on the precise control of particle size, morphology and chemical composition.

So far, several techniques have been used for preparation of HAp powder, which can be divided into two major routes: wet methods and solid state reaction. The wet methods include co-precipitation [7-9], hydrothermal process [10-12], mechanochemical method [13] and sol-gel synthesis [14,15]. Depending on the techniques used, HAp with various morphologies, composition, and crystalline degree have been obtained and shown to have different effects on the bioactivity, mechanical properties, and dissolution behavior in biological environment [16,17]. The hydrothermal technique usually gives HAp powders a high degree of crystallinity and a Ca/P ratio close to the stoichiometric value.

Olive oil is used as an additive which is mainly a triacylglyceride of long chain fatty acids with free fatty acids (FFA), polyphenols, peroxides, polycyclic aromatic hydrocarbons (PAHs), vitamin K and Vitamin E. The fatty acids present in olive oil are oleic acid, linoleic acid and linoolenic acid. Thus, in the present investigation olive oil assisted synthesis of HAp's was successfully performed.

2. Experimental

2.1 Materials

Calcium nitrate tetrahydrate ($Ca(NO_3)_2.4H_2O$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$) and ammonia solution were used as the starting materials. All chemicals used in this work were 98% purity purchased from Qualigens chemicals, India without any further purification. Olive oil was used as an additive.

2.2 Synthesis of nano-HAP

In this work, 1M calcium nitrate and 0.6M ammonium dihydrogen phosphate solutions were prepared in distilled water and ammonia solution was added till pH 11 was obtained. To the calcium nitrate

solution, olive oil (0, 10, 25 and 50 ml) was added and stirred under heating at 70 ºC for 1.5 h. To this mixture, ammonium dihydrogen phosphate solution was added drop-wise and stirred for 2 h. The resulting solution was then transferred to a Teflon-lined autoclave kept in a furnace at a temperature of 150 ºC for 5 h. After the hydrothermal treatment was over, the resulting suspension was filtered and washed with distilled water and acetone to remove the residual impurities and dried in an oven. The final product was sintered in a muffle furnace at 800 ºC for 2h. The white powder obtained was then finely grounded using mortar and pestle and used for further characterization. Olive oil assisted HAp's synthesized using 10, 25 and 50 ml of olive oil were designated as HO-10, HO-25, HO-50 respectively while those synthesized without the addition of olive oil was termed as HA.

2.3 Characterization studies

The functional group analysis of the HAp powders was carried out by Fourier transform infrared spectrometer (FT-IR, BRUKER TENSOR 27) after pelletizing them using KBr and tracing the FT-IR spectra in the transmittance mode from 400 to 4000 cm^{-1}. The phase content and crystallinity of the HAp powders were investigated using BRUKER D8 advance X-ray diffraction (XRD) measurement. The morphology of the synthesized HAp powders was assessed using a field emission scanning electron microscope (FE-SEM) coupled with energy dispersive X-ray analysis (FE-SEM/EDX, Hitachi SU6600).

3. Results and Discussion

3.1 FT-IR

The FT-IR spectra of pure HAp and olive oil assisted HAp are shown in Fig. 1. A band at 3571 cm^{-1} in the spectra shows the presence of stretching mode (υ_s) of hydroxyl group in the synthesized samples. The broad bands at 3437 and 1624 cm^{-1} are due to the adsorbed water molecules present in the HAp lattice. The peak at 961cm^{-1} is due to the non degenerated υ_1 symmetric stretching mode of P-O bonds of phosphate. The triply degenerated υ_3 asymmetric stretching mode of P-O bonds of phosphate is observed at 1035 and 1091cm^{-1}. The small peaks related to carbonate are appeared at 1419 and 1457 cm^{-1} are due to the exposure of the samples to atmosphere. All the observed peaks of the synthesized samples are matching with standard HAP.

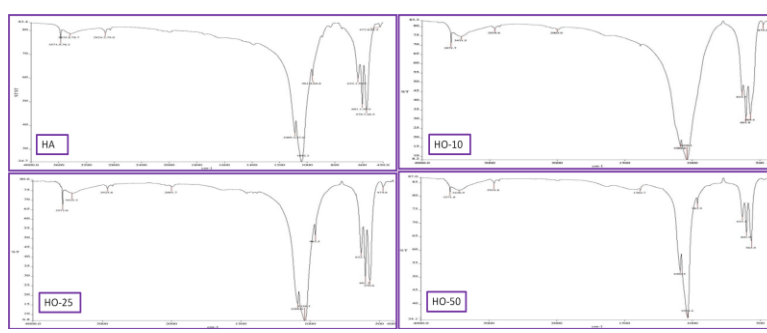

Fig. 1 FT-IR spectra of pure HAp and olive oil assisted HAp's

3.2XRD

The XRD patterns of pure HAp and olive oil assisted HAp's are shown in Fig. 2. All the synthesized samples are in good agreement with the standard JCPDS card (09-0432) for HAP. From the JCPDS, it was confirmed that the synthesized samples are in hexagonal phase with lattice parameters, a =9.4232 A° and c = 6.8833 A° (space group: P63/m) which indicates that the addition of olive oil does not induce any phase transformation in HAp. From the XRD patterns it can be observed that the crystallinity is increased with an increasing amount of olive oil from 10 to 50 ml.

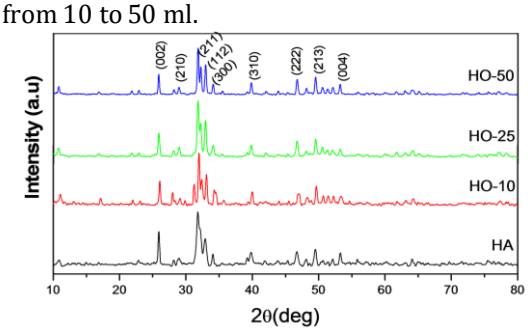

Fig. 2 XRD patterns of pure HAp and olive oil assisted HAp's

3.3FESEM/EDX

The morphological analysis of pure HAp and olive oil assisted HAp's are carried out by FE-SEM coupled with EDX analysis are shown in Fig. 3. Pure HAp shows spherical morphology with greater extent of agglomeration. Initially, the addition of olive oil does not indulge any change in morphology. But, the addition of higher content of olive oil changes the spherical structure to rod structure. Thus, it was evident that the additive (olive oil) played a significant role in changing the morphological features. The EDX spectrum reveals the presence of prominent elements present in HAp.

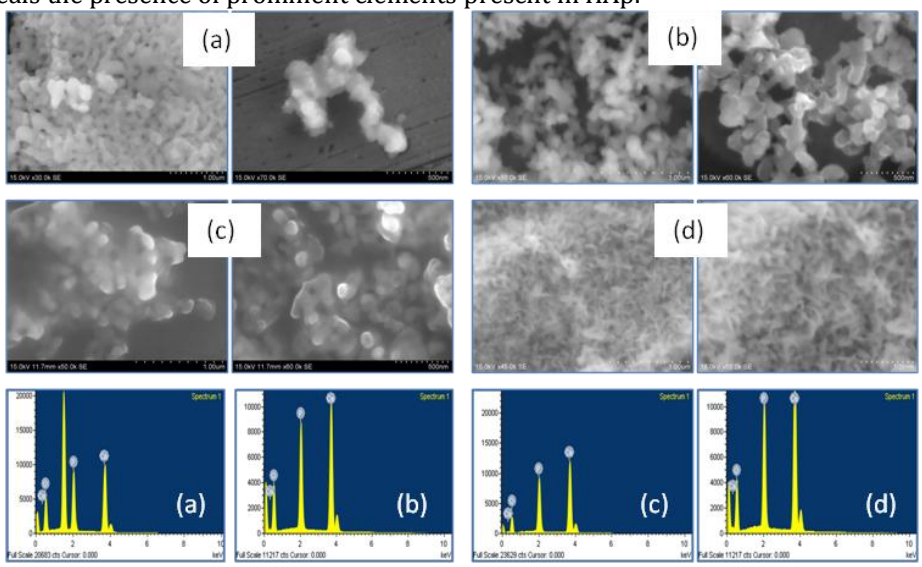

Fig. 3 FE-SEM images and the corresponding EDX patterns of pure HAp and olive oil assisted HAp's: (a) HA; (b) HO-10; (c) HO-25; and (d) HO-50

Conclusion

In this study, we reported the synthesis of hydroxyapatite using olive oil as an additive by hydrothermal method. From FT-IR spectra, it was confirmed that the functional groups present in the samples correspond to the hydroxyapatite. From XRD results, we observed that the addition of olive oil increases the crystallinity of HAp. The FESEM images of HAp without olive oil showed more agglomeration of particles and the morphological changes takes place from spherical to rod shape with the increased volume of olive oil addition.

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