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Synthesis and Spectroscopic Characterization of Hydroxyapatite by Sol-Gel Method

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Abstract: Hydroxyapatite (HAP) nanoparticles were synthesized by sol-gel method at 75°C. In this low temperature synthesized HAP nano particles were involved various biomedical applications like bone defects, bone augmentation, as well as implant coating. For this synthesized HAP were examined functional groups, microstructure and phase analysis by using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM). The XRD spectrum of dried HAP precursor confirms that crystallite size below 45 nm and FTIR spectrum conforms the functional groups of phosphate (PO_4^{3-}) and hydroxyl (O-H) groups, SEM images of HAP appears in a platelets shape, this platelets size in (30-75) nm.
Key words: XRD, SEM, agglomerated, platelets.

1. Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$,HAP) is the bioceramic material consists of calcium and phosphate minerals [1].HAP is most importance to synthesize nano-composites of organic and inorganic in order to have good biocompatibility, high bioactivity and great bonding properties[2]. However densified HA, fabricated with HA powders of large particle size, has low mechanical strength and fracture toughness on comparison with natural human bone, thus restricting their use to less stressful applications [3] and also using gas sensor application [4].HAP in an artificial implant is limited because of its fragility and poor mechanical Properties [5].It could be natural or synthetic, and it which has excellent biocompatibility with bones, teeth, skin and muscles, both in vitro and in vivo. HAP promotes faster bone regeneration, and direct bonding to regenerated bones without intermediate connective tissues[6].Synthesis of HAP in different techniques reported in literature including sol-gel[7],chemical precipitation[8],micro wave and ultrasonic irradiation[9,10],micro emulsion[11], molten salt method[12].among these methods two methods sol-gel and chemical precipitation based on aqueous media is evident that superior in synthesizing HAP with phase purity and desired morphology even at low temperature range from 40°C to 100°C[13].This bioceramic HAP material synthesized in several shapes and size like nano rods [14],nano fiber and plate[15,16], hollow spheres[17] and using different organic modifiers like Twee20,disodiumcitrate and polyethylene glycol[18] and EDTA and CTAB [19,20], etc. Hydroxyapatite coated Ti and other metals using in clinical application joint replacement and repair bone defects, bone replacement [21].

In this present work proceed over the synthesis of nanostructured hydroxyapatite by water based sol-gel method using calcium nitrate tetra hydrate and di-ammonium hydrogen phosphate are the starting reactants materials and ammonia solution used for pH adjustment for mixing of Ca and P solution.

2. Experimental

2.1. Materials and methods

Calcium nitrate tetra hydrate (Ca $(NO_3)_2.4H_2O$), di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) and ammonia solution were used to synthesis HAP nano particle, these analytical grade chemicals are purchased from Merck used without any further purification. In this synthesis 1M of calcium nitrate and 0.67M of di-ammonium hydrogen phosphate dissolved in double distilled water in room temperature. Phosphate solution added with drop by drop in calcium nitrate solution at temperature 75°C and pH was maintained at 11 for throughout the experiment using ammonia solution, these final mixers continuously stirred 12 hours, product allowed to cool for 24 hours. The aged gels washed with double distilled water and ethanol at least three times. Finally white product kept in hot air oven at 85°C for overnight, this experimental method as shown in the flow chart fig .1.

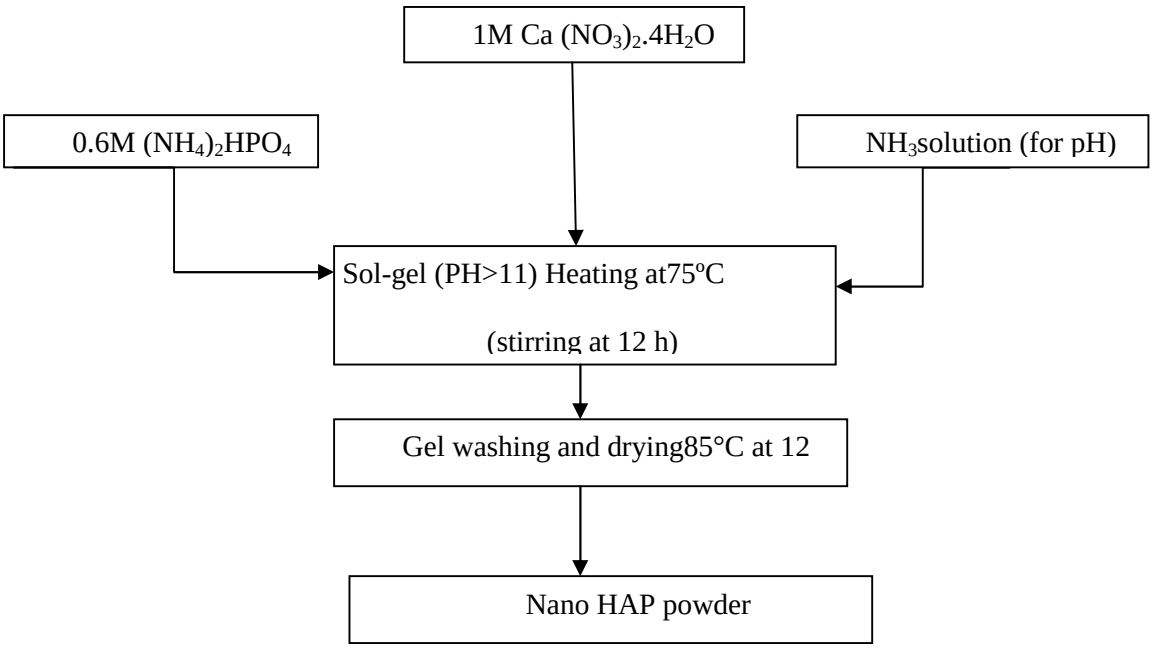


Fig.1:

2.2. Characterization Studies

Synthesized HAP powder characterized by XRD, FTIR and SEM to determine the fraction of crystallinity, crystallite size and specific surface area of the HAP sample using powder X-ray diffraction instrument D8 advnced BRUKER, Spectrometer using CuKα radiation source and its wave length (λ=1.54Å), data collected from the 2θ range from 20°to 60° in steps of 0.019° and count time 0.2S.The crystallite size of the sample was calculated from the Scherrer's equation [22].

$$X_S = \frac{0.9^{a}}{\cos^{=}} \qquad (1)$$

Where β is the full width half maximum under considerations of selected diffraction maximum intensity peaks in radian, λ is the wave length CuKα radiation source (λ=1.54Å) and θ is the angle of diffraction (°).The fraction of crystallinity (X_c) of the HAP nanoparticle calculated [23] from the equation

$$X_c = \left(0.24/\ \right)^3 \qquad (2)$$

Specific surface area of the HAP determined by the formula [24]

$$S = 6\times10^{3} / d^{\circ} \qquad (3)$$

Where ρ is the crystallite size (nm) and d is the theoretical density of HAP (3.16 g/cm^3).

Fourier transform infrared spectroscopy (FTIR) spectrum was recorded in the range of 4000-400cm^{-1} by using an instrument Perkin Elmer RXI FT-IR spectrometer by KBr pellet technique. The morphology of synthesized HAP sample was viewed by the Quanta 200 FEG scanning electron microscope (SEM) magnification range from 12x to greater than 1,00,000x.

3. Results and Discussion:

3.1. Powder X-ray diffraction analysis (XRD)

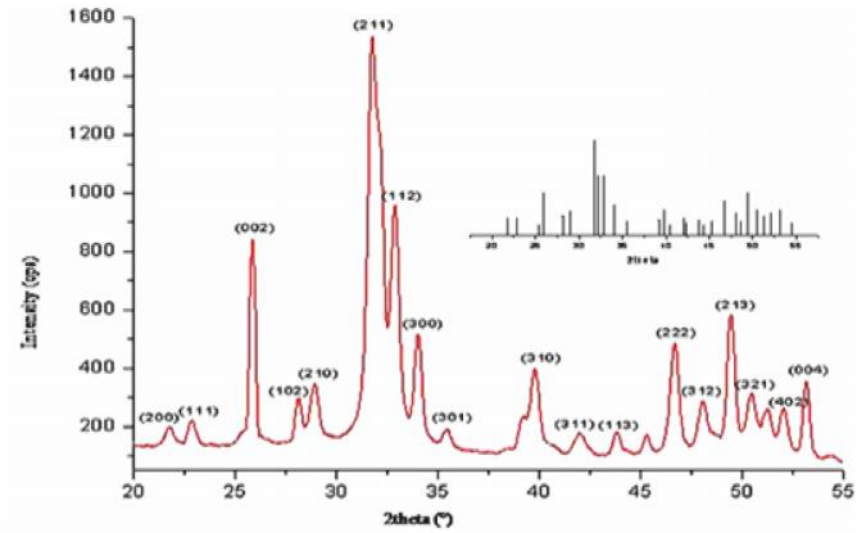


Fig.2: XRD spectrum of nano-HAP powder was synthesized by sol-gel method at 75°C .

Fig 2.shows that the collected XRD data was perfectly matched with standard ASTM data (JCPDS no 09-0432). crystallite size and crystallinity of hydroxyapatite were investigated with powder XRD spectrum and broaden diffraction peaks are 2θ=25.8, 31.7, 32.1and 32.9 these peaks are assigned to the miller's indices reflection planes are (002),(211),(112) and (300) indicates that the amorphous phase hydroxyapatite and crystallite size is very small from 25-60 nm, specific surface area range from 112 to 194 m^2g^{-1}.This XRD spectrum indicates most of the high intensity peaks positioned between2θ=25-34° and we observed that peak broadening was indicated synthesized HAP crystallite size present in nanoscale level without any other phase like TCP or CaO phase. Line width and crystallize size, fraction crystallinity, and specific surface area as shown in the table (1).

Table.1: Line width and crystallize size, fraction crystallinity, and specific surface area

Plane	Line width (FWHM)	2Theta	Crystallite size X_s(nm)	Fraction of crystallinity (X_c)	Specific surface area (m^2/g)
002	0.1973	25.8	41	1.799	46.310
211	0.2763	31.7	29	0.655	65.470
112	0.2170	32.1	38	1.352	49.966
300	0.2565	32.9	32	0.819	59.335

3.2. FT-IR functional group studies

Fig (3) indicates that the small characterized peaks are 3572 and 632 cm^{-1} assigned to hydroxyl (O-H) functional group. A next stretching vibration modes of PO_4^{3-} appears in 1093, 1033 and 962cm^{-1}, while other peaks are 603 and 565 cm^{-1} corresponding to the (P-O) bending modes of vibration. Wave number 1714 indicates that strong intensity of (C-O) stretching vibration modes.

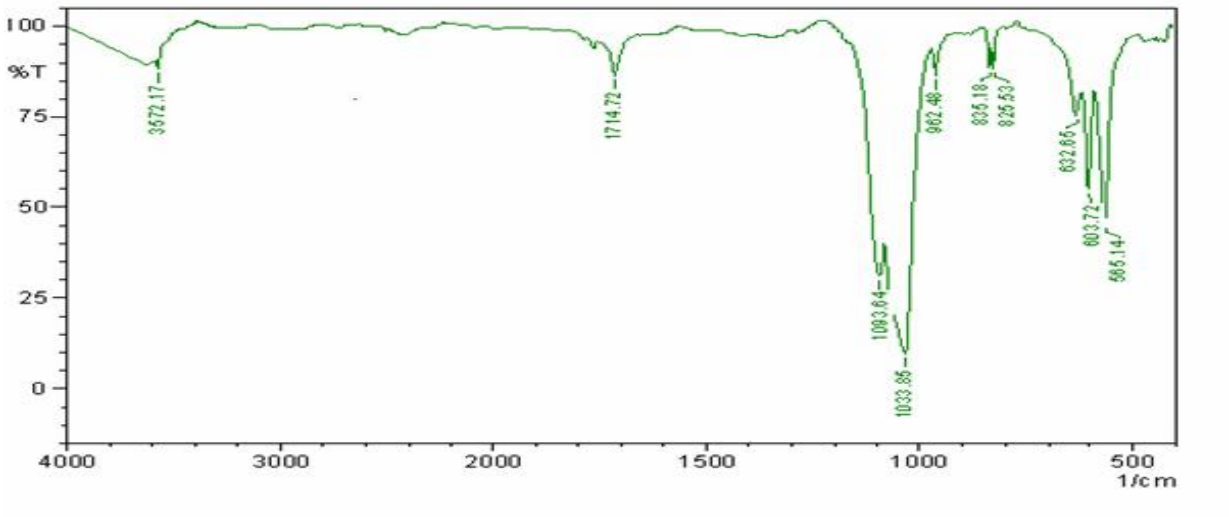
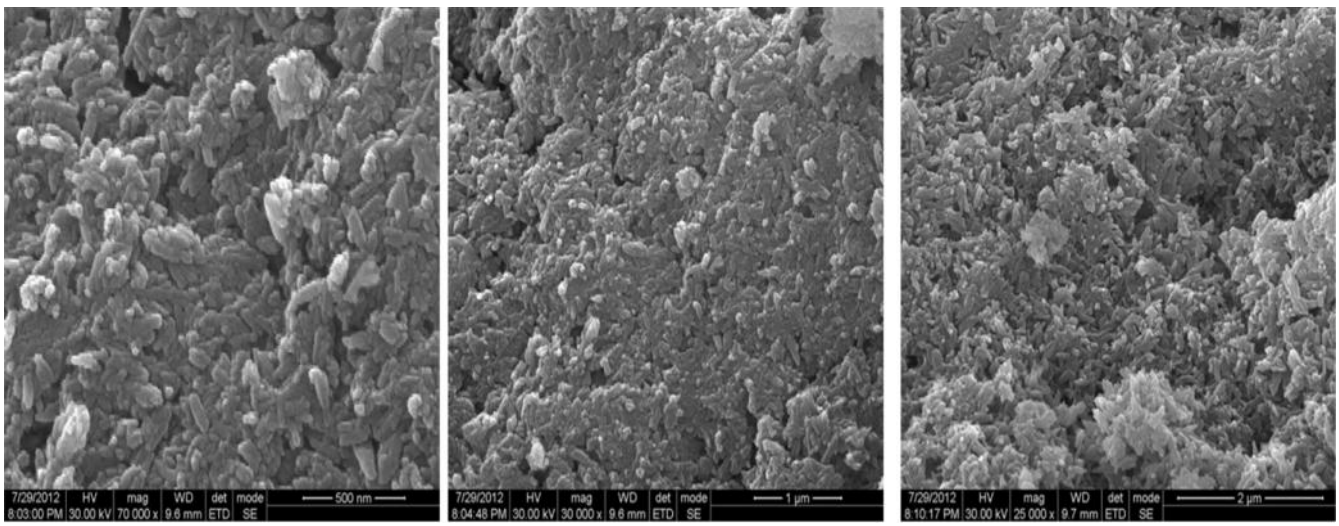


Fig.3 : FT-IR spectrum of nano-HAP powder was synthesized by sol-gel method at 75°C

3.3. Morphology analysis

The high resolution SEM image of HAP powder with various magnifications as shown in figure(3),this HAP powder images appears in clear with micro pores between the particle, definite shape and non-uniform platelets like morphology with particle size in range from 35 to 65 nm respectively. These pores are used for a flow of the physiological fluid the coatings when it is beneficial for the biomaterial in implantation of living things [16]**.**



4. Conclusion

This report hydroxyapatite platelets shape nano particle synthesis by sol-gel method. In this method very simple and water base process; gel formed without any external agent, synthesized powder without grating in nanoscale level. The nano-size has been finding XRD, FESEM micrographs .XRD spectra shows particle size about 30 to 65 nm and specific surface area of the HAP lies between 46 to 59 m^2/g. FTIR result conforms functional groups like(C-O),(O-H)and (P-O).FESEM micrograph illustrated nanoscale HAP and appear the agglomeration. Sol-gel method is simple, low cost effect and also nanoparticle produced large scale in the coating purpose.

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