Influence of surfactant on synthesis of HAp by hydrothermal route

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ABSTRACT

Hydroxyapatite (Ca_{10} (PO_4)$_6$ (OH) $_2$: HAp) is the principle inorganic constituent in bone and hence widely used ceramic biomaterials. To effectively control the processing parameters several investigations have been made. With such a wide variety of methods for the synthesis of HAp nanoparticles, choosing a definite procedure to synthesize a well distinct powder can be difficult. In general, it is suitable to control the crystal size of materials using surfactant aided routes. Hence, in our present investigation we try to synthesis HAp crystals using surfactant aided method. The effect on morphology of HAp using a cationic surfactant cetyl trimethyl ammonium bromide (CTAB) by hydrothermal reactions is discussed. These crystals were characterized for crystallinity, stoichiometric ratio, and crystalline size.

Keywords: Hydroxyapatite, Hydrothermal, Surfactant, CTAB, crystal size.
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INTRODUCTION

Hydroxyapatite [$Ca10(PO_4)_6(OH)_2$, HAp], the prime integrant, constituting nearly 65 wt% in bone and teeth, has attracted a great deal of attention in biomedical applications due to its close similarity in chemical composition with natural bone[1]. Biocompatibility, biological activity, osteo-inductivity, osteo-conductivity, osseo-integration, stable bioresorption, strong ion exchange capacity and ability to promote bone ingrowths besides aiding regeneration of new bones are among the most important properties of HAp [1-4]. Consequently, used as dental filler material, bone & bone graft substitutes in orthopedic applications, hard tissue paste, tissue engineering, biological sensors and drug carriers [5-7]. Furthermore, HAp has also been studied for other non-medical applications, such as packing media for column chromatography, gas sensors, catalysts, etc. [2, 9]. Hence, Synthesis of synthetic HAp with similar properties to that of natural one is the most explored topic of extensive biological and physico-chemical research. In recent times to boost the biological activity of hydroxyapatite, the control of size, particle agglomeration, shape and stoichiometric is essential [2-3]. Therefore, a number of dispensation routes have been urbanized for the preparation of hydroxyapatite, which includes sol-gel processing, co-precipitation technique, emulsion, hydrothermal synthesis, mechano-chemical methods and chemical vapour deposition [4-8]. The limitations of these methods often include (i) precise control over reaction conditions, (ii) large amounts of toxic organic solvents. However, their physical properties such as fracture toughness and fracture strength depend on the crystal structure, composition and sizes [10]. Therefore it becomes crucial to essentially control crystallite size, agglomeration surface area, shape, etc. The use of surfactants in the synthesis of HAp is advisable to produce lesser agglomerated particles. Surfactants are usually organic compounds that are amphiphllic, containing both hydrophobic and hydrophilic groups Hence, soluble in both organic solvents and water. In the field of pharmaceutical sciences , the surfactants are used as emulsifiers , wetting agents solubilizers etc. The use of a simple cationic Surfactants cetyltrimethylammonium bromide (CTAB) in controlling, the morphology and size of HAp is implemented here using hydrothermal synthesis.

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EXPERIMENTAL SECTION

HAp nanopowders were synthesized using the micelle as a template system where the mixture of cetyltrimethyl ammonium bromide (CTAB) as the template. Analytical grade Calcium nitrate (Ca $(NO_3)_2 \cdot 4H_2O$) and diamonium hydrogen phosphate $(NH_4)_2HPO_4$) were used as precursors for calcium and phosphate, respectively. Along with this, Analytical grade ammonia and CTAB were also used in the synthesis of HAp. A solution of 0.6M $(NH_4)_2HPO_4$ and 0.1M CTAB were dissolved in 50 ml of double distilled water. The solution was stirred for 30 min with a magnetic stirrer to ensure that the cooperative interaction and self-assembly process were completed. Then, 1 mole $Ca(NO_3)_2 \cdot 4H_2O$ dissolved in 50 ml of distilled water . Then the Ca $(NO_3)_2 \cdot 4H_2O$ solution were added to the latter drop wise under continuous stirring, pH of the solution was adjusted to 9 using ammonia solution. The final milky suspension was transferred to an autoclave, hydrothermally treated in an oven at 180 °C for 24 h. The resulting precipitates was washed and then oven dried at 100°C for 20 hours .and further calcinated in a furnace at 800∘C for 2 hours, yielding Hydroxyapatite powder.
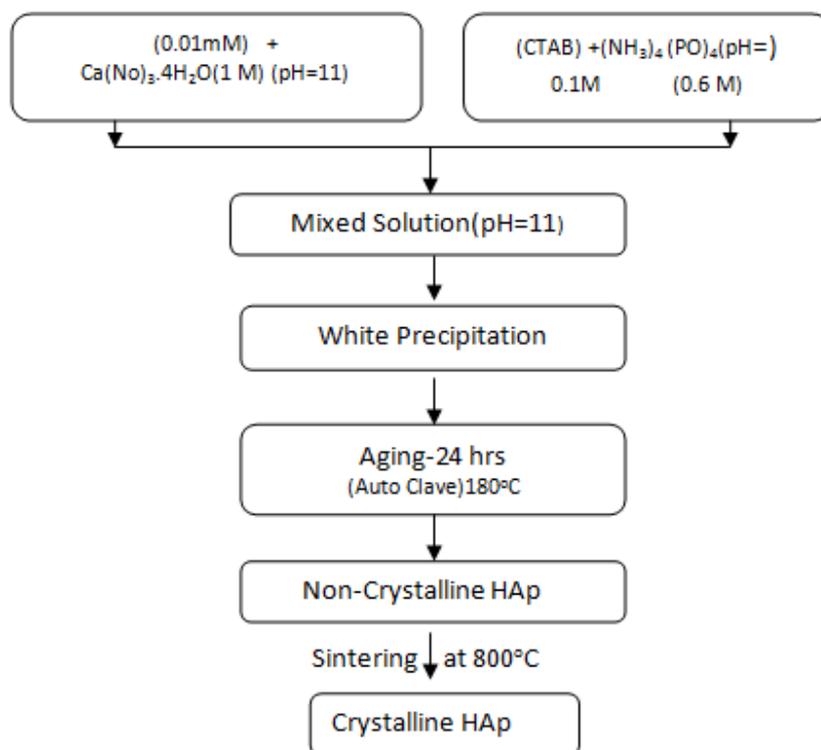

Figure 1: Flow chart of synthesis of HAp

The morphologies of the as-prepared HAP were observed by a scanning electron microscopy (FESEM: Supra VP35 Carl Zeiss, Germany) .The energy dispersive X-ray (EDX: X-Max, USA) spectra were obtained by a standard unit (Oxford Instruments, UK) attached to the FESEM. The phase analysis of the HAp powder was analyzed with X-ray diffractometer (X'pertPro, Philips, Netherlands). The 2Ө scanning range was from 10°-90° with step time of 1 sec and step size of 2Ө=0.1°. The Fourier transform infrared (FTIR) spectroscopy (shimadzu, KBr pellet technique) were used to identify the functional groups present in hydroxyapatite.

RESULTS AND DISSUSSION

The XRD pattern of HAp sample synthesized is shown in figure.2. For comparison HAP powder samples were also prepared without using surfactant hydrothermally. The diffraction patterns shows sharp and clear reflections however with varying intensity which confirms the phase purity and crystallinity associated with each of the samples. The XRD pattern, with major diffraction peaks located at 2θ = 25.9° (002), 2θ = 31.7 (211), 2θ = 32.1 (112), 2θ = 32.8(300), 2θ = 46.6(222) and 2θ = 49.4 (213) are found to match with ICDD - PDF2 card: 00-009-

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0432. These data confirm that the major phase as hydroxyapatite particles .No other phases was observed in the XRD pattern, signifying the chief inorganic phase of the sample is HAP crystal. The particle size D_{hkl} and the degree of crystallinity (X_c) is evaluated based on the previous reports [11] by equation (1) & (2) as follows,

$$D_{hkl} = K\lambda / \beta \cos\theta \qquad (1)$$

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

Where: $K = 0.94$ is a constant; λ is the wavelength of monochromatic radiation($\lambda = 1.5405\text{Å}$); β is defined as diffraction peak width at half height, expressed in radians, at maximum intensity at $2\theta = 39.75$ corresponding to phase (211). The crystalline size of samples without CTAB was 45.86 nm and that synthesized with is 39.1nm with a crystallinity of 1.39.and 1.13 respectively. The FTIR spectra of the samples were shown in Figure 3. It exposed the characteristic transmittance bands of Hydroxyapatite from 4000 cm^{-1} to 650cm^{-1}. The Characteristics band at 1035cm^{-1} is assigned due to $\nu1$ vibration mode of the phosphate group. The Characteristics band at 1085 $cm^{-1}$and 968 cm^{-1} is due to $\nu1$ vibration mode of the phosphate group [12, 13]. The peak at 3569 cm^{-1} is typical stretching vibration modes confirming the presence of hydroxyl ion in the apatite lattice [14]. The FT-IR results clearly indicate that CTAB functional groups are not incorporated in the HAp.
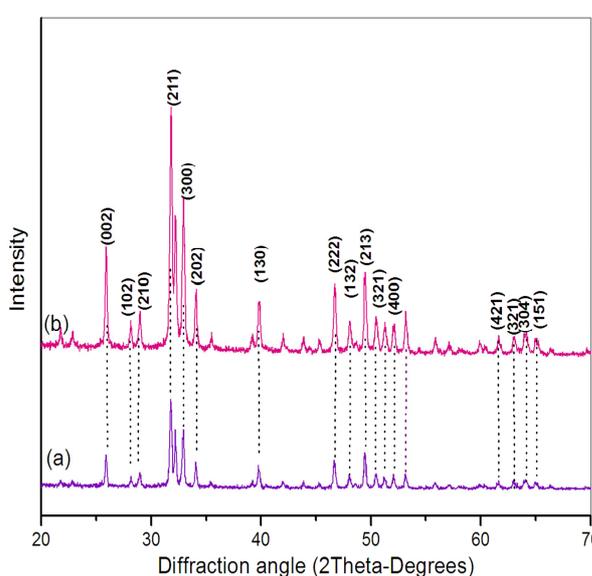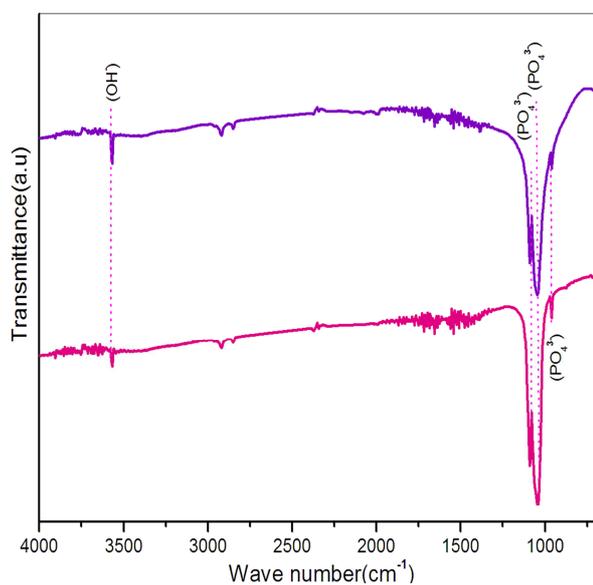

Figure 2: XRD patern of (a)Pure HAp (b)With CTAB
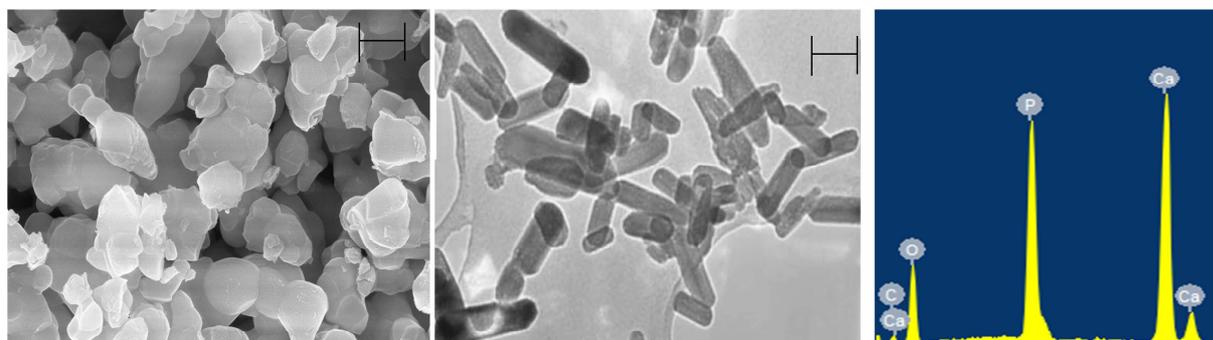

Figure 3: FTIR of (a)Pure HAp (b)With CTAB

Figure 4 : FESEM of HAp synthesized Without and with CTAB & EDAX

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To screen the influence of surfactants on the morphology and size of HAp particles, the synthesis process was conducted with and without CTAB. The SEM image of the sample synthesized at 150 °C in the absence and those obtained at 180 °C in the presence of CTAB is shown Figure4. As shown in the Fig. 4, in the absence CTAB, the HAp particles showcases larger particles with irregular shape (spherical, needle and quasi spherical) agglomerated non-uniformly 50–200 nm. On the other hand, from the SEM photographs of HAp powders synthesized at 180 °C in the presence of surfactants , the HAp particles have uniform, long, rod-like morphology with the typical diameter of about 40–100 nm. Shanti et al. (2009) obtained hydroxyapatite rods with diameter 20 nm and length in the range of 100–120 μm using only cationic surfactant (CTAB)[15]. Yan et al. (2001) used an anionic surfactant (SDS) as regulator of the nucleation and crystal growth in the synthetic method of preparing HA. The obtained hydroxyapatite had particles of nanorods structure (150 nm/10 nm)[8]. Liu et al. (2004) synthesized HA nanorods of 50–80 nm in diameter and 0.5–1.2 μm in length using surfactants of CTAB and PEG 400. These methods inhibit the excess agglomeration of the particles, since the surfactants can adsorb on the surface of particles. The EDAX analysis reveals an highly stoichiometric (Ca/P = 1.68) HAp with high degree of crystallinity.

CONCLUSION

It is well known that the hydrothermal temperature plays a key role in the controlling the crystallite size, degree of crystallinity and the stoichiometric ratio [8, 12]. However, the obtained powders were highly agglomerated and their size distribution is comparatively large. Hence surfactant aided route is best used to synthesize nanopowders, nanorods and nanoneedles [11, 8, 13]. Thus, Hydrothermal synthesis using CTAB as soft template can effectively control the morphology Also, the effect on the composition, crystallite size and stoichiometry of hydroxyapatite particles is investigated.

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